Supplementary Materials for

Oxidative Aliphatic C-H Fluorination with Fluoride Ion Catalyzed by a Manganese Porphyrin

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Oxidative Aliphatic C-H Fluorination with Fluoride Ion Catalyzed by a Manganese Porphyrin

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Supporting Online Materials

General information. All fluorination reactions were run under nitrogen with no precautions taken to exclude moisture. All solvents were purified according to the method of Grubbs.(*45*) 5,10,15,20-Tetramesitylporphyrinatomanganese(III) chloride [Mn^{III}(TMP)Cl] was prepared by metallation of tetramesitylporphyrin. Iodosylbenzene was prepared by hydrolysis of iodobenzene diacetate with sodium hydroxide solution. Bicyclo[4.1.0] heptane (norcarane) was prepared according to a literature method.(*46*) Other purchased materials were of the highest purity available from Aldrich and used without further purification. GC/MS analyses were performed on an Agilent 7890A gas chromatograph equipped with an Agilent 5975 mass selective detector. ^{1}H NMR spectra were obtained on a Varian INOVA 400 (400 Hz) or a Bruker Avance 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at δ 7.26). Data reported as: chemical shift (δ or ppm), multiplicity (s= singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz); integrated intensity. Proton decoupled ^{13}C NMR spectra were recorded at 125 MHz on a Bruker Avance 500 spectrometer and are reported in ppm using solvents as an internal standard ($CDCl_3$ at 77.15 ppm). ^{19}F NMR spectra were obtained at 375 MHz on a Varian INOVA 400 spectrometer and are reported in ppm by adding external neat PhF (^{19}F, δ -113.15 relative to $CFCl_3$)

General procedures for Mn(TMP)F catalyzed C-H bond Fluorinations

An oven-dried 25 mL Schlenk flask equipped with a magnetic stir bar was charged with the following: the pre-catalyst, Mn(TMP)Cl (**1**) (13.2 mg, 0.015 mmol, 1 mol%), TBAF•$3H_2O$ (0.3 mmol), AgF (4.5 mmol, 3 equiv.), substrate (1.5 mmol) and naphthalene (internal standard, 0.5 mmol). Under these conditions the UV-vis λ_{max} observed for (TMP)Mn^{III}–Cl (475 nm) changed

immediately to that of a 1:2 mixture of (TMP)Mn^{III}–F (453 nm) and [(TMP)$Mn^{III}(F)_2$]$^-$ (440 nm). The flask was capped and purged with nitrogen for 5 min. Then, CH_3CN (1.5 mL) and CH_2Cl_2 (0.5 mL) were added by syringe and the flask was heated at 50 °C in an oil bath. Iodosylbenzene (6-15 mmol, 4-10 equiv.) was added slowly to the reaction mixture in solid form over a period of 6-15 h. Significant decreases in yield were noted when the iodosylbenzene was added rapidly. Much shorter reaction times (1-2 hr) could be achieved at higher temperatures. With mCPBA as the oxidant, up to 40% yields could be obtained within 1 hr. Each addition of 1 equiv. oxidant was followed by Mn(TMP)Cl (13.2 mg, 1 mmol%) added dissolved in minimal amount of solvents. When the reaction was completed, the solution was allowed to cool to room temperature and was then passed through a short pad of silica gel (washing with dichloromethane). The filtrate was analyzed by GC/MS and then concentrated under vacuum. Products were separated from the reaction residue by column chromatography.

Fluorination of hydrocarbons (Table 1. Entry 1-5, Figure 2A)

The reaction was run according to the general procedure above using the hydrocarbon listed as the substrate. When the reaction was completed, the solution was allowed to cool to room temperature and was then passed through a short pad of silica gel (washing with dichloromethane). The filtrate was analyzed by GC/MS. The assignment of the products was based on the comparison of GC retention time and mass fragmentation with the authentic samples. The products of *trans*-decalin fluorination were assigned by comparing the GC retention time with authentic samples, prepared by treating corresponding alcohols with DAST.

Fluorination of norcarane (Table 1. Entry 6)

The reaction was run according to the general procedure above using bicyclo[4.1.0] heptane (norcarane) as a substrate (*2*) and 0.5 equiv. iodosylbenzene as the oxidant. When the reaction was completed, the solution was allowed to cool to room temperature and was then passed through a short pad of silica gel (washing with dichloromethane). The filtrate was analyzed by GC/MS. The rearranged product, 3-fluoromethylcyclohexene, was identified by the characteristic m-CH_2F peak in the mass spectrum.

Kinetic isotope effect of the fluorination reaction

The reaction was run according to the general procedure above using cyclohexane/cyclohexane-d_{12} (1:1) or ethylbenzene/ethylbenzene-d_{10} (1:1) as the substrate and 0.5 equiv. iodosylbenzene as the oxidant. When the reaction was completed, the solution was allowed to cool to room temperature and was then passed through a short pad of silica gel (washing with dichloromethane). The filtrate was analyzed by GC/MS. The kinetic isotope effect was determined by calculating the ratio of corresponding peak intensities (82/92 $[M\text{-}HF]^+$ for cyclohexane/cyclohexane-d_{12} and 105/114 $[M\text{-}F]^+$ for ethylbenzene/ethylbenzene-d_{15}).

Preparation of $Mn^{IV}(TMP)F_2$

$Mn^{IV}(TMP)F_2$ was prepared by treating $Mn^{IV}(TMP)Cl_2$, prepared as previously reported (*36*), with excess silver fluoride. In a typical experiment, silver fluoride (1.6 mmol) was added in solid form to a solution of $Mn^{IV}(TMP)Cl_2$ (30 mg, 0.033 mmol) in 1.5 mL benzene. The reaction was stirred vigorously at room temperature. After 2 hours, the solution was filtered to remove the insoluble silver salts, and the filtrate was concentrated under vacuum. The purple solid thus obtained was redissolved in 0.5 mL of benzene and the solution was filtered again. The solvent was removed under vacuum to afford $Mn^{IV}(TMP)F_2$ as a purple solid (24 mg, 84% yield). The shiny purple crystals suitable for X-ray crystal structure analysis were grown by the diffusion of a pentane layer (3 mL) into 0.5 mL benzene solution at 2°C (Tables S1-S5).

Reaction of azo-bis-α-phenylethane with $Mn^{IV}(TMP)F_2$

The thermal decomposition of azo-bis-α-phenylethane was conducted at 105 °C in the presence of freshly prepared $Mn^{IV}(TMP)F_2$. In a typical experiment, silver fluoride (1.6 mmol) was added in solid form to a solution of $Mn^{IV}(TMP)Cl_2$ (30 mg, 0.033 mmol) in 1.5 mL benzene-d_6. The reaction mixture was stirred vigorously at room temperature. After 2 hours, the solution was filtered into a 4 mL vial, and azo-bis-α-phenylethane (3 mg, 0.4 equiv) was added to the filtrate. The solution was degassed by three freeze-pump-thaw cycles and was then heated at 105 °C for 4 min. The vial was then cooled to room temperature and the yield of (1-fluoroethyl)benzene was determined by ^{19}F NMR (δ, -167.2 ppm) using trifluorotoluene as the internal standard.

Single turnover fluorination of cyclooctane with $Mn^{IV}(TMP)F_2$

The single turnover fluorination reaction was carried out in the presence of Mn(TMP)Cl with $Mn^{IV}(TMP)F_2$ in place of silver fluoride. In a typical experiment, an oven-dried 25 mL Schlenk flask equipped with a magnetic stir bar was charged with the following: Mn(TMP)Cl (30 mg, 0.034 mmol), TBAF•$3H_2O$ (0.3 mmol) and $Mn^{IV}(TMP)F_2$ (30 mg, 0.034 mmol. The flask was capped and purged with nitrogen for 5 min. Then, CH_3CN (1.5 mL) and CH_2Cl_2 (0.5 mL) containing cyclootane (1.5 mmol) were added via syringe and the flask was heated at 50 °C in an oil bath. Iodosylbenzene (11 mg, 0.05 mmol) was added in one portion to the mixture and the reaction was stirred for 30 minutes. The solution was allowed to cool to room temperature and was then passed through a short pad of silica gel (washing with dichloromethane). The filtrate was analyzed by GC/MS and the yield of cyclooctyl fluoride (43%) was calculated based on $Mn^{IV}(TMP)F_2$ loaded using ethylbenzene as an internal standard. There was negligible fluorination under these conditions without $Mn^{IV}(TMP)F_2$.

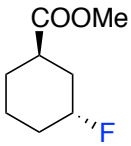


Table 1, Compound 8. The reaction was run according to the general procedure above using methyl cyclohexanecarboxylate as the substrate. Purification by column chromatography (hexanes and then 5% EtOAc/hexanes). The regiochemical assignment was made on the basis of the unsymmetrical ^{13}C NMR. The stereochemical assignment was made on the basis of the obvious vicinal, trans-diaxial H-F J-coupling and small vicinal H-H couplings (δ 4.85, dtt, J=47.7, 5.7, 2.3 Hz) (Figs. S1-S3). ^{1}HNMR (500 MHz, $CDCl_3$) δ 4.85 (dt, J=47.7, 2.3 Hz, 1H), 3.61 (s, 3H), 2.67 (tt, J=11.6, 3.8 Hz, 1H), 2.11 (m, 1H), 1.89 (m, 2H), 1.72-1.38 (m, 5H). ^{13}C APT NMR (125 MHz, $CDCl_3$) 176, 88.6, 51.8, 37.8, 33.1, 30.2, 28.1, 19.6 ppm. ^{19}F NMR -183.0 ppm. MS (EI) m/z cal'd $C_8H_{13}FO_2$ $[M]^+$: 160.1, found 160.1.

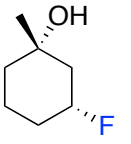


Table 1. Compound 9. The reaction was run according to the general procedure above using methyl cyclohexanol as a substrate. Purification by column chromatography (hexanes and then 10% ethyl acetate/hexanes). The regiochemical assignment was made on the basis of the unsymmetrical ^{13}C NMR. The stereochemical assignment was made on the basis of the obvious J-coupling between the fluorine and the

hydroxyl proton, δ 2.50 (d, J=10.7 Hz) (Figs. S4-S6). ^{1}HNMR (500 MHz, $CDCl_3$) δ 4.86 (dtt, J=48.1, 5.3, 2.9 Hz, 1H), 2.50 (d, J=10.7 Hz, 1H), 1.97 (m, 1H), 1.84 (m, 2H), 1.64 (m, 2H), 1.41 (m, 3H), 1.14 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 91.6, 42.8, 38.4, 30.4, 29.7, 16.7 ppm. ^{19}F NMR -179.2 ppm. MS (EI) m/z cal'd $C_7H_{13}FO$ $[M]^+$: 132.1 found 132.1.

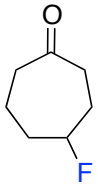


Table 1. Compound 10. The reaction was run according to the general procedure above using methyl cycloheptanone as a substrate. Purification by column chromatography (hexanes and then 4% ethyl acetate/hexanes). The regiochemical assignment was made on the basis of the three-bond F-C_2 coupling, 36.4 ppm (d, J=8.7 Hz) (Figs. S7-S9). ^{1}HNMR (500 MHz, $CDCl_3$) δ 4.75 (dtt, J=45.6, 7.4, 2.7 Hz, 1H), 2.73, (m, 1H), 2.49, (m, 1H), 2.40 (m, 1H), 2.30 (ddd, J=15.4, 9.2, 2.5 Hz, 1H), 2.08-1.76 (m, 5H). 1.58 (m, 1H). ^{13}C APT NMR (125 MHz, $CDCl_3$) 91.7, 43.5, 36.4, 35.4, 29.7, 17.6 ppm. ^{19}F NMR -175.3 ppm. MS (EI) m/z cal'd $C_7H_{11}FO$ $[M]^+$: 130.1, found 130.1.

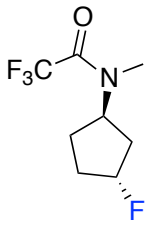


Table 1. Compound 11. The reaction was run according to the general procedure above using N-methyl-trifluoroacetylcyclopentylamine as the substrate. Purification by column chromatography (hexanes and then 4% ethyl acetate/hexanes). The regiochemical assignment was made the on the basis of the two-bond F-C_2 coupling, 36.7 ppm (d, J=22.0 Hz). The stereochemical assignments were made on the basis of the ^{19}FNMR chemical shifts. The *cis*-isomer (-171.0 ppm) exhibits a smaller upfield shift than the *trans*-isomer (168.8) due to the shielding of the fluorine by the amide group (Figs. S10-S12). For *trans*-**11**: ^{1}HNMR (500 MHz, $CDCl_3$) δ 5.13-4.39 (m, 2H), 2.93 (d, 3H), 2.23 (dddd, J=35.8, 15.9, 10.6, 5.0 Hz, 1H), 2.07 (m, 1H), 1.96-1.71 (m, 3H), 1.67-1.49 (m, 1H). ^{13}C APT NMR (125 MHz, $CDCl_3$)157.2, 116.5, 94.5, 56.4, 54.0, 36.7, 35.5, 32.9, 29.0, 27.5, 25.8 ppm. ^{19}F NMR -68.7 (s), -70.2 (s), -168.8 (m) ppm. MS (EI) m/z cal'd $C_7H_{11}FO$ $[M]^+$: 213.1, found 213.1.

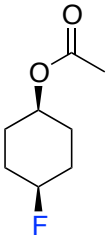


Table 1. Compound 12a (cis). The reaction was run according to the general procedure above using cyclohexylacetate as a substrate. Purification by column chromatography (1% ethyl acetate/petroleum ether). The regiochemical assignment

was made the on the basis of the symmetric ^{13}C NMR. The stereochemical assignment was made on the basis of the obvious vicinal, trans-diaxial H-F J-coupling and the small vicinal H-H coupling, δ 4.63 (dtt, J=52.1, 5.8, 2.9 Hz) (Figs. S13-S15). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.75-4.57 (m, 2H), 1.99 (s, 3H), 1.93 (m, 2H), 1.74 (m, 2H), 1.68-1.57 (m, 4H). ^{13}C APT NMR (125 MHz, $CDCl_3$) 170.7, 88.7, 70.6, 28.9 26.6, 21.5 ppm. ^{19}F NMR -180.4 ppm. MS (EI) m/z cal'd $C_8H_{12}O_2$ $[M-HF]^+$: 140.1, found 140.1.

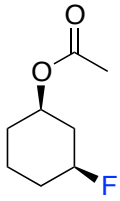


Table 1. Compound 12b (cis). The regiochemical assignment was made the on the basis of the unsymmetrical ^{13}C NMR. The stereochemical assignment was made on the basis of the H-F J-coupling and the large vicinal H-H coupling, δ 4.48 (dtt, J=48.0, 10.1, 4.4 Hz, 1H) (Figs. S16-S17). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (m, 1H), 4.48 (dtt, J=48.0, 10.1, 4.4 Hz, 1H), 2.28 (m, 1H), 2.04-1.93 (m, 2H), 1.98 (s, 3H). 1.81 (m, 2H), 1.60-1.40 (m, 3H), ^{13}C APT NMR (125 MHz, $CDCl_3$) 170.5, 89.5, 69.9, 37.9, 31.5, 30.5, 21.4, 18.8 ppm. ^{19}F NMR -180.4 ppm. MS (EI) m/z cal'd $C_8H_{12}O_2$ $[M-HF]^+$: 140.1, found 140.1.

Compounds **12a** (trans) and Compound **12b** (trans) were isolated as an inseparable mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07-5.46 (m, 2H), 1.97 (s, 3H), 1.95-1.32 (m, 8H). ^{19}F NMR -180.0, -181.1 ppm.

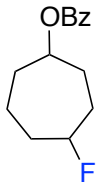
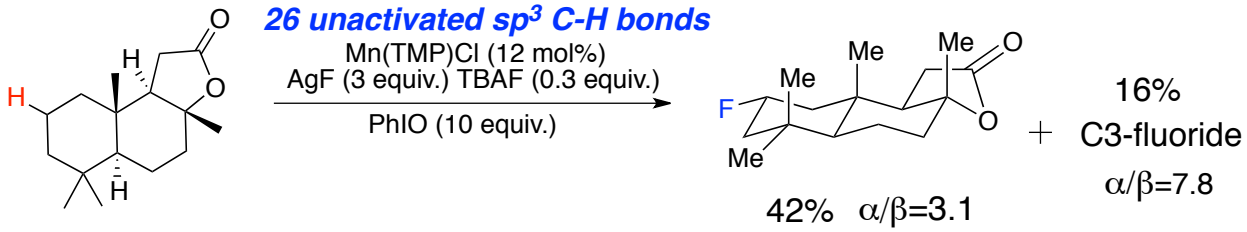


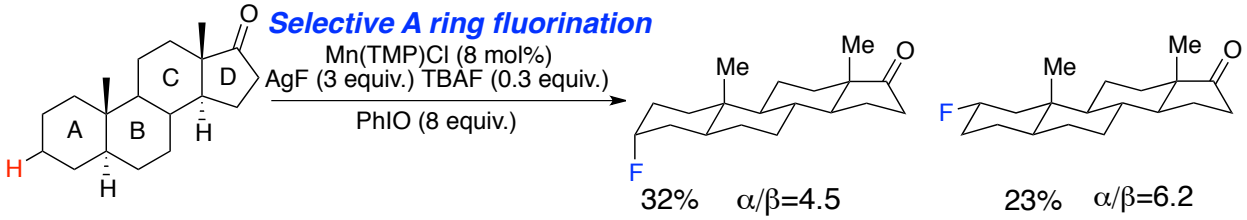
Table 1. Compound 13. The reaction was run according to the general procedure above using cycloheptyl benzoate as the substrate. Purification by column chromatography (hexanes and then 1% ethyl acetate/hexanes) and products isolated as a mixture of cis and trans isomers. The regiochemical assignment was made the on the basis of the three-bond F-C_2 coupling, 26.6 ppm (d, J=10.0 Hz). Fig. S18; $^{1}HNMR$ (500 MHz), $CDCl_3$) δ 7.96 (m, 2H), 7.49 (m, 2H), 7.38 (m, 1H), 5.20-4.70 (m, 2H). 2.50-1.50 (m, 10H). ^{19}F NMR -164.6, -166.7 ppm. MS (EI) m/z cal'd $C_{14}H_{17}FO_2$ $[M]^+$: 236.1, found 236.1.

Fig. 2B. Sclareolide fluorination:



Reaction was run according to the general procedure above using sclareolide as a substrate. After the reaction was over, the mixture was subjected to the workup protocol outlined in the general procedure and purified by column chromatography (hexanes and then 10% EtOAc/hexanes). The assignment of the product structures was based on the diagnostic F-NMR spectrum. 2α (-180.3 ppm, dm), 2β (-172.6 ppm, qt), 3α (-187.8 ppm, qt), 3β (-185.6 ppm, dm). The major 2α-fluoro isomer could be isolated a white solid on a second column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (dtt, J=48.0, 11.3, 4.6 Hz, 1H), 2.45 (dd, J=16.2, 14.7 Hz, 1H), 2.27 (dd, J=15.8, 6.5 Hz, 1H), 2.12-1.85 (m, 6H), 1.70 (td, J=12.6, 4.1 Hz, 1H), 1.43-1.30 (m, 6H), 0.99 (s, 3H), 0.95 (s, 3H), 0.89 (s, 3H); ^{19}F NMR -180.3 ppm (Figs. S23-S26). MS (EI) m/z cal'd $C_{16}H_{25}FO_2$ $[M]^+$: 268.2, found 268.2.

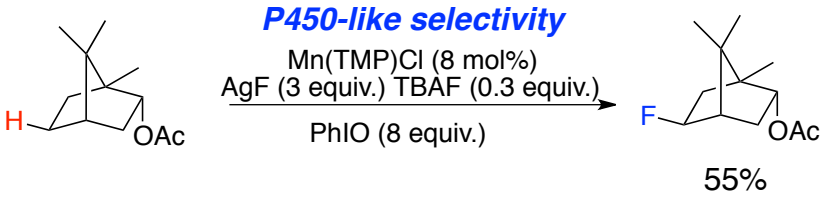
Fig. 2C. 5α-Androstan-17-one fluorination:



Reaction was run according to the general procedure above using 5α-Androstan-17-one as a substrate. After the reaction was over, the mixture was subjected to the workup protocol outlined in the general procedure and purified by column chromatography (hexanes and then 30% DCM/hexanes). The assignment of the product structures was based on the diagnostic F-NMR spectrum. 2α (-172.4 ppm, dm), 2β (-172.8 ppm, qt), 3α (-181.5 ppm, qt), 3β (-168.3 ppm, dm). The major product 3α-fluoro-5α-Androstan-17-one was isolated by a second column chromatography (4% ethyl acetate/hexanes). ^{1}HNMR (500 MHz, $CDCl_3$) δ 4.75 (dm, J=48.7, 2.5 Hz, 1H), 2.37 (dd, J=19.1, 8.9 Hz, 1H), 2.01 (dt, J=19.4, 9.1 Hz, 1H), 1.85 (m, 2H), 1.73 (m, 2H), 1.60 (m, 3H), 1.53-1.32 (m, 6H), 1.28-1.09 (m, 6H) 0.95 (m, 1H), 0.79 (s, 3H), 0.74 (s, 3H).

^{13}C APT NMR (125 MHz, $CDCl_3$) 221.6, 89.4, 54.2, 51.4, 47.8, 39.4, 35.9, 35.0, 33.9, 32.4, 31.5, 30.8, 28.0, 27.1, 21.8, 20.1, 13.9, 11.2 ppm. ^{19}F NMR -181.5 ppm. MS (EI) m/z cal'd $C_{19}H_{29}FO$ $[M]^+$: 292.2, found 292.2 (Figs. S19-S22).

Fig. 2D. Bornyl-acetate Fluorination:



Reaction was run according to the general procedure above using bornyl acetate as a substrate. After the reaction was over, the mixture was subjected to the workup protocol outlined in the general procedure and purified by column chromatography using DCM:hexanes (1:4) as eluent. The product was obtained in 55% yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (d, J=9.7 Hz, 1H), 4.56 (ddd, J=60, 7.6, 2.3 Hz, 1H), 2.33 (m, 2H), 2.05-1.95 (m, 1H) 1.98 (s, 3H), 1.63 (dd, J=35.3, 15.4 Hz, 1H), 0.97 (s, 3H), 0.85 (s, 3H), 0.83 (s, 3H), 0.68 (dd, J=14.5, 3.4 Hz, 1H). ^{13}C APT NMR (125 MHz, $CDCl_3$) 95.8 (d, 186 Hz), 77.6, 50.5 (d, 17.6 Hz), 37.5 (d, 18.0 Hz), 32.2 (d, 11.1 Hz), 21.3, 20.2, 19.4, 12.6 ppm. ^{19}F NMR -158.2 ppm (Figs. S27-S30). MS (EI) m/z cal'd $C_{12}H_{19}FO_2$ $[M]^+$: 214.1, found 214.1.

Computational details

The geometry optimizations and zero-point vibrational energy (ZPVE) were carried out using the B3LYP(*47-49*) functional with the 6-31G**(*50, 51*) basis set for all atoms except Mn. For Mn the first two shells of core electrons were described by the Los Alamos angular momentum projected effective core potential (ECP) using the double-ζ contraction of valence functions(*52*) (denoted as LACVP**) leading to 15 explicit electrons for neutral Mn. In order to obtain a more accurate electronic energy, we performed single-point energy calculations using a larger basis set, where Mn was described with the triple-ζ contraction of valence functions augmented with two f functions(*53*) (the core electrons were described by the same ECP), with the other atoms described with the 6-311++G**(*54, 55*) basis set.

Solvation energies Gsolv were calculated using the Poisson-Boltzmann self-consistent polarizable continuum method(*56, 57*) implemented in Jaguar to represent CH3CN (dielectric constant = 36.7 and effective radius = 2.23 Å). The solvation calculations used the B3LYP/LACVP** level of theory and the gas-phase optimized structures. Enthalpies are

$$H_{298K} = E_{elec} + G_{solv} + ZPVE + \sum_{\nu} \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{n}{2} kT \,,$$

where ZPVE is the zero-point vibrational energy, n = 12 accounts for the potential and kinetic energies of the translational and rotational modes, and T = 298 K. Coordinates are listed in Table S6.

All calculations performed with the Jaguar package.(*58*)

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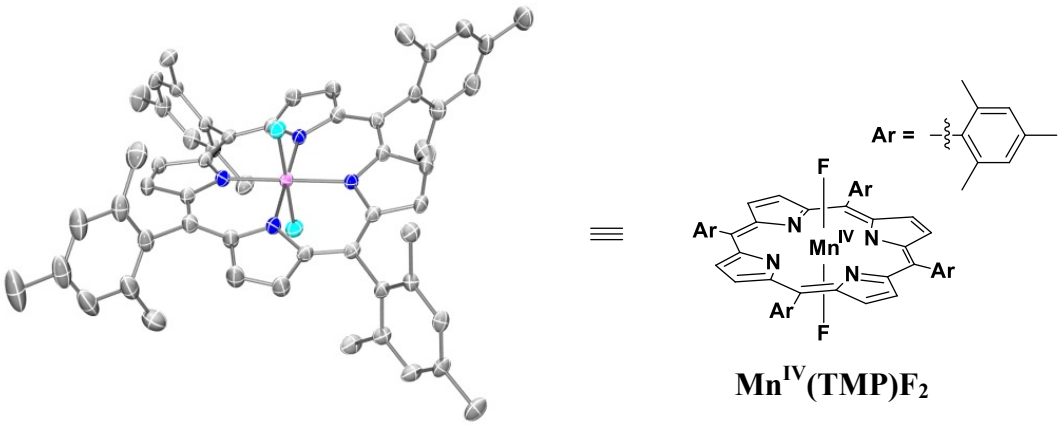

$Mn^{IV}(TMP)F_2$

Table S1. Crystal data for $Mn^{IV}(TMP)F_2$

Empirical formula	$C_{61}H_{64}F_2MnN_4$
Formula weight	946.10
Temperature	100 K
Wavelength	Cu *K*α radiation, λ = 1.54184 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit Cell dimensions	*a* = 23.5969 (3) Å

	b = 16.1927 (2) Å
	c = 26.6602 (3) Å
Volume	10186.8 (2) Å^3
Z	8
Density (calculated)	1.234 Mg/m^3
Absorption coefficient	2.50 mm^{-1}
F(000)	4008
Crystal size	0.17 × 0.10 × 0.05 mm
Theta range for data collection	3.7 to 65.6°
Index ranges	h = -26→27, k = -18→14, l = -31→20
Reflection collected	38219
Independent reflections	8519 [R_{int} = 0.029]
Absorption correction	multi-scan *SADABS* V2008/1 (Bruker AXS)

Table S2. Structural refinement details for $Mn^{IV}(TMP)F_2$

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.157
S = 1.07
Data completeness = 0.958
8519 reflections
614 parameters
3 restraints
Least-squares matrix: full
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 11.7278P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rangle_{max}$ = 0.69 e Å^{-3}
$\Delta\rangle_{min}$ = -0.55 e Å^{-3}

Table S3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.11386 (11)	0.14479 (17)	0.33652 (11)	0.0242 (6)	
C2	0.11470 (13)	0.16475 (18)	0.38899 (11)	0.0307 (7)	
H2	0.1213	0.2177	0.4031	0.037*	
C3	0.10437 (14)	0.09461 (19)	0.41445 (12)	0.0347 (7)	
H3	0.1013	0.0894	0.4498	0.042*	
C4	0.09887 (12)	0.02909 (18)	0.37866 (11)	0.0274 (6)	
C5	0.09474 (12)	-0.05381 (18)	0.39073 (11)	0.0277 (6)	
C6	0.10008 (11)	-0.11720 (17)	0.35588 (11)	0.0245 (6)	
C7	0.10417 (12)	-0.20346 (17)	0.36842 (11)	0.0268 (6)	
H7	0.0990	-0.2270	0.4007	0.032*	
C8	0.11672 (11)	-0.24464 (17)	0.32592 (11)	0.0256 (6)	
H8	0.1231	-0.3024	0.3230	0.031*	
C9	0.11873 (11)	-0.18532 (16)	0.28581 (11)	0.0228 (6)	
C10	0.12585 (11)	-0.20468 (16)	0.23518 (10)	0.0223 (6)	
C11	0.11763 (11)	-0.14751 (16)	0.19691 (11)	0.0224 (6)	
C12	0.11561 (12)	-0.16776 (17)	0.14473 (11)	0.0279 (6)	
H12	0.1234	-0.2202	0.1304	0.033*	
C13	0.10057 (12)	-0.09873 (17)	0.11952 (11)	0.0287 (7)	
H13	0.0949	-0.0942	0.0844	0.034*	
C14	0.09486 (11)	-0.03386 (17)	0.15556 (11)	0.0237 (6)	
C15	0.08578 (11)	0.04920 (17)	0.14378 (10)	0.0233 (6)	
C16	0.09018 (11)	0.11282 (17)	0.17861 (10)	0.0225 (6)	
C17	0.09135 (12)	0.19889 (17)	0.16573 (11)	0.0259 (6)	
H17	0.0839	0.2219	0.1336	0.031*	
C18	0.10495 (11)	0.24102 (17)	0.20767 (11)	0.0244 (6)	
H18	0.1105	0.2990	0.2102	0.029*	
C19	0.10957 (11)	0.18231 (16)	0.24780 (11)	0.0228 (6)	
C20	0.11893 (11)	0.20206 (16)	0.29799 (11)	0.0230 (6)	
C21	0.08629 (14)	-0.07724 (18)	0.44461 (11)	0.0325 (7)	
C22	0.13186 (17)	-0.0760 (2)	0.47813 (13)	0.0449 (9)	
C23	0.1208 (2)	-0.0944 (2)	0.52888 (14)	0.0568 (11)	
H23	0.1511	-0.0919	0.5523	0.068*	
C24	0.0672 (2)	-0.1161 (2)	0.54571 (14)	0.0533 (10)	
C25	0.02393 (18)	-0.1195 (2)	0.51131 (13)	0.0500 (10)	
H25	-0.0127	-0.1359	0.5222	0.060*	
C26	0.03205 (15)	-0.09985 (19)	0.46119 (12)	0.0392 (8)	

C27	0.19128 (17)	-0.0573 (3)	0.46045 (16)	0.0636 (12)
H27A	0.1998	-0.0904	0.4306	0.095*
H27B	0.2183	-0.0708	0.4871	0.095*
H27C	0.1943	0.0015	0.4521	0.095*
C28	0.0567 (2)	-0.1341 (3)	0.60099 (15)	0.0789 (16)
H28A	0.0913	-0.1230	0.6201	0.118*
H28B	0.0460	-0.1922	0.6051	0.118*
H28C	0.0260	-0.0988	0.6133	0.118*
C29	-0.01759 (15)	-0.1038 (2)	0.42573 (14)	0.0495 (9)
H29A	-0.0167	-0.1562	0.4074	0.074*
H29B	-0.0154	-0.0578	0.4019	0.074*
H29C	-0.0530	-0.0999	0.4448	0.074*
C30	0.14224 (11)	-0.29133 (17)	0.22179 (11)	0.0235 (6)
C31	0.19835 (12)	-0.30634 (17)	0.20641 (11)	0.0283 (6)
C32	0.21484 (13)	-0.38722 (19)	0.19693 (12)	0.0355 (7)
H32	0.2529	-0.3977	0.1872	0.043*
C33	0.17770 (14)	-0.45315 (18)	0.20115 (13)	0.0360 (7)
C34	0.12173 (13)	-0.43666 (17)	0.21462 (12)	0.0315 (7)
H34	0.0955	-0.4810	0.2166	0.038*
C35	0.10340 (12)	-0.35697 (18)	0.22528 (11)	0.0258 (6)
C36	0.24035 (12)	-0.23710 (19)	0.20061 (14)	0.0373 (8)
H36A	0.2788	-0.2599	0.1990	0.056*
H36B	0.2374	-0.1996	0.2294	0.056*
H36C	0.2323	-0.2066	0.1697	0.056*
C37	0.19775 (17)	-0.5402 (2)	0.19171 (16)	0.0548 (10)
H37A	0.2392	-0.5423	0.1942	0.082*
H37B	0.1861	-0.5576	0.1581	0.082*
H37C	0.1811	-0.5773	0.2167	0.082*
C38	0.04199 (12)	-0.34293 (18)	0.23839 (12)	0.0324 (7)
H38A	0.0202	-0.3338	0.2076	0.049*
H38B	0.0387	-0.2944	0.2601	0.049*
H38C	0.0271	-0.3915	0.2559	0.049*
C39	0.07586 (12)	0.07132 (17)	0.08996 (11)	0.0260 (6)
C40	0.02067 (13)	0.08639 (18)	0.07321 (11)	0.0307 (7)
C41	0.01220 (14)	0.1070 (2)	0.02312 (12)	0.0381 (8)
H41	-0.0253	0.1171	0.0117	0.046*
C42	0.05670 (15)	0.11307 (19)	-0.01061 (11)	0.0369 (8)
C43	0.11079 (15)	0.0983 (2)	0.00694 (12)	0.0397 (8)

H43	0.1417	0.1023	-0.0158	0.048*
C44	0.12175 (13)	0.0779 (2)	0.05645 (12)	0.0344 (7)
C45	-0.02871 (13)	0.0816 (2)	0.10875 (13)	0.0452 (9)
H45A	-0.0232	0.0353	0.1319	0.068*
H45B	-0.0637	0.0734	0.0897	0.068*
H45C	-0.0313	0.1332	0.1279	0.068*
C46	0.04583 (18)	0.1363 (2)	-0.06454 (13)	0.0537 (10)
H46A	0.0808	0.1298	-0.0839	0.081*
H46B	0.0332	0.1938	-0.0663	0.081*
H46C	0.0164	0.1002	-0.0785	0.081*
C47	0.18165 (14)	0.0647 (3)	0.07408 (14)	0.0540 (10)
H47A	0.2080	0.0768	0.0466	0.081*
H47B	0.1864	0.0072	0.0847	0.081*
H47C	0.1896	0.1015	0.1024	0.081*
C48	0.13808 (12)	0.28774 (16)	0.31105 (10)	0.0238 (6)
C49	0.19555 (12)	0.29832 (18)	0.32335 (11)	0.0285 (6)
C50	0.21605 (13)	0.37758 (18)	0.33253 (12)	0.0327 (7)
H50	0.2550	0.3847	0.3405	0.039*
C51	0.18119 (13)	0.44613 (17)	0.33028 (11)	0.0295 (7)
C52	0.12419 (12)	0.43418 (17)	0.31932 (11)	0.0274 (6)
H52	0.0997	0.4807	0.3185	0.033*
C53	0.10182 (11)	0.35620 (17)	0.30953 (10)	0.0234 (6)
C54	0.23520 (13)	0.22550 (19)	0.32702 (14)	0.0382 (8)
H54A	0.2745	0.2449	0.3253	0.057*
H54B	0.2279	0.1874	0.2992	0.057*
H54C	0.2290	0.1969	0.3589	0.057*
C55	0.20475 (15)	0.53180 (19)	0.33902 (14)	0.0416 (8)
H55A	0.1865	0.5708	0.3160	0.062*
H55B	0.2457	0.5315	0.3330	0.062*
H55C	0.1973	0.5486	0.3737	0.062*
C56	0.03908 (12)	0.34751 (18)	0.29984 (12)	0.0295 (7)
H56A	0.0230	0.3071	0.3232	0.044*
H56B	0.0330	0.3287	0.2653	0.044*
H56C	0.0205	0.4011	0.3047	0.044*
F1	0.18031 (7)	0.00291 (9)	0.26553 (6)	0.0303 (4)
F2	0.02844 (7)	-0.00880 (9)	0.26887 (6)	0.0268 (4)
Mn1	0.104423 (18)	-0.00215 (2)	0.267055 (16)	0.01964 (14)
N1	0.10448 (9)	0.06158 (14)	0.33122 (9)	0.0239 (5)

N2	0.10835 (9)	-0.10800 (14)	0.30514 (9)	0.0227 (5)	
N3	0.10522 (9)	-0.06505 (13)	0.20276 (9)	0.0217 (5)	
N4	0.10012 (9)	0.10423 (14)	0.22892 (8)	0.0206 (5)	
C5S	0.1719 (3)	0.3139 (5)	0.0583 (3)	0.147 (3)	
H5S1	0.1517	0.2843	0.0317	0.220*	
H5S2	0.1558	0.3694	0.0620	0.220*	
H5S3	0.1679	0.2837	0.0900	0.220*	
C3S	0.2296 (6)	0.2838 (8)	-0.0047 (4)	0.261 (5)	
H3S1	0.1990	0.3097	-0.0245	0.313*	
H3S2	0.2243	0.2232	-0.0032	0.313*	
C1SA	0.3319 (11)	0.3596 (19)	-0.0222 (11)	0.147 (3)	0.44 (3)
H1S1	0.3205	0.4114	-0.0062	0.220*	0.44 (3)
H1S2	0.3439	0.3706	-0.0568	0.220*	0.44 (3)
H1S3	0.3635	0.3351	-0.0035	0.220*	0.44 (3)
C1SB	0.3509 (8)	0.3235 (17)	-0.0099 (9)	0.147 (3)	0.56 (3)
H1S4	0.3603	0.3818	-0.0150	0.220*	0.56 (3)
H1S5	0.3747	0.2892	-0.0317	0.220*	0.56 (3)
H1S6	0.3576	0.3086	0.0252	0.220*	0.56 (3)
C2S	0.2903 (6)	0.3096 (8)	-0.0225 (5)	0.261 (5)	
H2S1	0.3109	0.2582	-0.0140	0.313*	
H2S2	0.2844	0.3056	-0.0592	0.313*	
C4S	0.2369 (5)	0.3209 (7)	0.0441 (4)	0.261 (5)	
H4S1	0.2504	0.3787	0.0424	0.313*	
H4S2	0.2617	0.2880	0.0665	0.313*	

Table S4. Atomic displacement parameters (Å^2) for $Mn^{IV}(TMP)F_2$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0237 (14)	0.0190 (14)	0.0300 (16)	-0.0011 (11)	-0.0018 (12)	-0.0020 (12)
C2	0.0425 (18)	0.0216 (15)	0.0280 (16)	0.0000 (13)	-0.0013 (13)	-0.0039 (13)
C3	0.053 (2)	0.0279 (16)	0.0235 (16)	-0.0016 (14)	-0.0004 (14)	-0.0040 (13)
C4	0.0353 (16)	0.0235 (15)	0.0234 (16)	-0.0013 (12)	-0.0007 (12)	-0.0002 (13)
C5	0.0313 (15)	0.0248 (15)	0.0269 (16)	-0.0003 (12)	-0.0015 (12)	0.0012 (13)
C6	0.0250 (14)	0.0219 (14)	0.0265 (16)	-0.0001 (12)	-0.0009 (11)	0.0029 (12)

C7	0.0322 (15)	0.0223 (14)	0.0259 (15)	0.0001 (12)	0.0011 (12)	0.0057 (13)
C8	0.0262 (14)	0.0181 (13)	0.0326 (17)	0.0012 (12)	-0.0015 (12)	0.0033 (13)
C9	0.0202 (13)	0.0167 (13)	0.0315 (16)	-0.0004 (11)	-0.0007 (11)	0.0016 (12)
C10	0.0185 (13)	0.0177 (13)	0.0307 (16)	-0.0020 (11)	0.0015 (11)	-0.0004 (12)
C11	0.0215 (13)	0.0178 (13)	0.0279 (15)	-0.0009 (11)	0.0026 (11)	-0.0012 (12)
C12	0.0347 (16)	0.0201 (14)	0.0289 (16)	0.0009 (12)	0.0025 (13)	-0.0043 (13)
C13	0.0381 (17)	0.0231 (15)	0.0250 (16)	-0.0020 (13)	0.0006 (12)	-0.0026 (13)
C14	0.0257 (14)	0.0214 (14)	0.0242 (15)	-0.0016 (12)	0.0016 (11)	-0.0006 (12)
C15	0.0232 (14)	0.0210 (14)	0.0256 (15)	0.0015 (11)	0.0005 (11)	0.0012 (12)
C16	0.0224 (13)	0.0192 (13)	0.0258 (15)	0.0003 (11)	0.0021 (11)	0.0017 (12)
C17	0.0282 (15)	0.0208 (14)	0.0285 (16)	0.0006 (12)	0.0012 (12)	0.0047 (13)
C18	0.0260 (14)	0.0174 (13)	0.0299 (16)	-0.0016 (11)	0.0020 (12)	0.0025 (12)
C19	0.0191 (14)	0.0178 (14)	0.0313 (16)	-0.0003 (11)	-0.0002 (11)	-0.0003 (12)
C20	0.0199 (13)	0.0186 (13)	0.0307 (16)	0.0006 (11)	0.0013 (11)	-0.0010 (12)
C21	0.0508 (19)	0.0207 (14)	0.0261 (16)	0.0031 (14)	0.0013 (14)	0.0001 (13)
C22	0.069 (2)	0.0337 (18)	0.0323 (19)	0.0040 (17)	-0.0105 (17)	0.0026 (15)
C23	0.097 (3)	0.038 (2)	0.035 (2)	0.009 (2)	-0.024 (2)	0.0007 (17)
C24	0.097 (3)	0.0322 (19)	0.0302 (19)	0.016 (2)	0.008 (2)	0.0019 (16)
C25	0.075 (3)	0.0385 (19)	0.036 (2)	0.0126 (19)	0.0163 (19)	0.0080 (17)
C26	0.056 (2)	0.0288 (16)	0.0325 (18)	0.0071 (15)	0.0102 (15)	0.0033 (14)
C27	0.060 (3)	0.068 (3)	0.063 (3)	-0.007 (2)	-0.027 (2)	0.011 (2)
C28	0.148 (5)	0.053 (3)	0.035 (2)	0.033 (3)	0.017 (3)	0.011 (2)
C29	0.046 (2)	0.051 (2)	0.052 (2)	-0.0016 (17)	0.0116 (17)	0.0093 (19)
C30	0.0255 (14)	0.0180 (14)	0.0272 (15)	0.0003 (11)	-0.0002 (12)	0.0010 (12)
C31	0.0293 (15)	0.0227 (14)	0.0329 (16)	0.0015 (12)	0.0038 (12)	0.0004 (13)
C32	0.0347 (17)	0.0297 (16)	0.0422 (19)	0.0092 (14)	0.0071 (14)	-0.0001 (15)
C33	0.0469 (19)	0.0194 (15)	0.0418 (19)	0.0070 (14)	0.0049 (15)	0.0007 (14)
C34	0.0415 (17)	0.0175 (14)	0.0356 (18)	-0.0047 (13)	-0.0004 (14)	0.0019 (13)

C35	0.0302 (16)	0.0208 (14)	0.0263 (15)	-0.0025 (12)	-0.0029 (12)	0.0013 (12)
C36	0.0261 (16)	0.0334 (17)	0.052 (2)	-0.0010 (13)	0.0049 (14)	0.0028 (16)
C37	0.070 (3)	0.0247 (17)	0.070 (3)	0.0138 (17)	0.011 (2)	-0.0030 (18)
C38	0.0277 (16)	0.0268 (15)	0.0427 (19)	-0.0029 (13)	0.0005 (13)	-0.0004 (14)
C39	0.0360 (16)	0.0171 (13)	0.0249 (15)	-0.0023 (12)	0.0007 (12)	0.0002 (12)
C40	0.0376 (16)	0.0279 (15)	0.0266 (16)	-0.0038 (13)	-0.0017 (13)	0.0046 (13)
C41	0.0438 (18)	0.0393 (18)	0.0314 (17)	-0.0072 (15)	-0.0087 (14)	0.0066 (15)
C42	0.057 (2)	0.0291 (16)	0.0250 (16)	-0.0107 (15)	-0.0025 (15)	0.0026 (14)
C43	0.051 (2)	0.0375 (18)	0.0305 (18)	-0.0057 (16)	0.0108 (15)	0.0032 (15)
C44	0.0398 (17)	0.0336 (17)	0.0298 (17)	0.0012 (14)	0.0052 (13)	0.0023 (14)
C45	0.0340 (17)	0.064 (2)	0.0375 (19)	0.0013 (17)	-0.0016 (14)	0.0140 (18)
C46	0.077 (3)	0.056 (2)	0.0282 (19)	-0.016 (2)	-0.0031 (18)	0.0073 (17)
C47	0.0395 (19)	0.076 (3)	0.046 (2)	0.0050 (19)	0.0116 (16)	0.015 (2)
C48	0.0282 (15)	0.0176 (13)	0.0257 (15)	-0.0026 (11)	-0.0010 (12)	-0.0008 (12)
C49	0.0249 (14)	0.0244 (15)	0.0361 (17)	0.0013 (12)	-0.0011 (12)	-0.0020 (13)
C50	0.0269 (15)	0.0265 (15)	0.0449 (19)	-0.0042 (12)	-0.0029 (13)	-0.0059 (14)
C51	0.0340 (16)	0.0194 (14)	0.0350 (17)	-0.0050 (12)	0.0032 (13)	-0.0030 (13)
C52	0.0329 (15)	0.0188 (14)	0.0306 (16)	0.0036 (12)	0.0060 (12)	-0.0004 (12)
C53	0.0249 (14)	0.0224 (14)	0.0229 (15)	0.0015 (11)	0.0018 (11)	0.0010 (12)
C54	0.0275 (16)	0.0272 (16)	0.060 (2)	0.0043 (13)	-0.0065 (15)	-0.0027 (16)
C55	0.047 (2)	0.0231 (16)	0.055 (2)	-0.0071 (15)	0.0039 (17)	-0.0081 (16)
C56	0.0269 (15)	0.0263 (15)	0.0354 (17)	0.0030 (12)	-0.0002 (13)	-0.0002 (14)
F1	0.0249 (9)	0.0285 (9)	0.0375 (10)	-0.0011 (7)	-0.0016 (7)	0.0012 (7)
F2	0.0246 (9)	0.0214 (8)	0.0344 (9)	0.0003 (6)	-0.0008 (7)	0.0005 (7)
Mn1	0.0217 (2)	0.0146 (2)	0.0226 (3)	-0.00021	-0.00085	0.00028

				(17)	(17)	(18)
N1	0.0272 (12)	0.0180 (11)	0.0264 (13)	-0.0006 (9)	-0.0015 (10)	0.0005 (10)
N2	0.0254 (12)	0.0179 (11)	0.0249 (13)	0.0011 (9)	-0.0009 (9)	-0.0003 (10)
N3	0.0236 (12)	0.0182 (11)	0.0235 (12)	-0.0014 (9)	0.0001 (9)	0.0006 (10)
N4	0.0204 (11)	0.0174 (11)	0.0240 (13)	0.0003 (9)	-0.0011 (9)	0.0004 (10)
C5S	0.101 (5)	0.171 (7)	0.169 (7)	-0.001 (4)	0.028 (4)	-0.029 (6)
C3S	0.382 (14)	0.170 (6)	0.230 (9)	-0.100 (7)	-0.090 (9)	0.025 (6)
C1SA	0.101 (5)	0.171 (7)	0.169 (7)	-0.001 (4)	0.028 (4)	-0.029 (6)
C1SB	0.101 (5)	0.171 (7)	0.169 (7)	-0.001 (4)	0.028 (4)	-0.029 (6)
C2S	0.382 (14)	0.170 (6)	0.230 (9)	-0.100 (7)	-0.090 (9)	0.025 (6)
C4S	0.382 (14)	0.170 (6)	0.230 (9)	-0.100 (7)	-0.090 (9)	0.025 (6)

Table S5. Bond lengths (Å) and angles (º) for $Mn^{IV}(TMP)F_2$

Bond lengths (Å)			
C1—N1	1.373 (3)	C26—C29	1.506 (5)
C1—C20	1.389 (4)	C30—C35	1.407 (4)
C1—C2	1.436 (4)	C30—C31	1.407 (4)
C2—C3	1.345 (4)	C31—C32	1.390 (4)
C3—C4	1.433 (4)	C31—C36	1.504 (4)
C4—N1	1.376 (4)	C32—C33	1.386 (4)
C4—C5	1.384 (4)	C33—C34	1.394 (4)
C5—C6	1.390 (4)	C33—C37	1.508 (4)
C5—C21	1.499 (4)	C34—C35	1.390 (4)
C6—N2	1.375 (4)	C35—C38	1.508 (4)
C6—C7	1.440 (4)	C39—C40	1.398 (4)
C7—C8	1.348 (4)	C39—C44	1.408 (4)
C8—C9	1.438 (4)	C40—C41	1.391 (4)
C9—N2	1.376 (3)	C40—C45	1.504 (4)
C9—C10	1.396 (4)	C41—C42	1.386 (5)
C10—C11	1.391 (4)	C42—C43	1.380 (5)
C10—C30	1.499 (4)	C42—C46	1.508 (4)
C11—N3	1.376 (3)	C43—C44	1.385 (5)
C11—C12	1.430 (4)	C44—C47	1.505 (5)
C12—C13	1.352 (4)	C48—C53	1.401 (4)
C13—C14	1.430 (4)	C48—C49	1.406 (4)
C14—N3	1.378 (4)	C49—C50	1.393 (4)

C14—C15	1.398 (4)	C49—C54	1.508 (4)
C15—C16	1.391 (4)	C50—C51	1.383 (4)
C15—C39	1.497 (4)	C51—C52	1.390 (4)
C16—N4	1.369 (4)	C51—C55	1.513 (4)
C16—C17	1.436 (4)	C52—C53	1.393 (4)
C17—C18	1.348 (4)	C53—C56	1.510 (4)
C18—C19	1.435 (4)	F1—Mn1	1.7931 (17)
C19—N4	1.379 (3)	F2—Mn1	1.7968 (16)
C19—C20	1.393 (4)	Mn1—N3	1.994 (2)
C20—C48	1.500 (4)	Mn1—N2	1.994 (2)
C21—C22	1.398 (5)	Mn1—N1	1.998 (2)
C21—C26	1.403 (5)	Mn1—N4	2.003 (2)
C22—C23	1.410 (5)	C5S—C4S	1.584 (9)
C22—C27	1.510 (5)	C3S—C4S	1.444 (9)
C23—C24	1.387 (6)	C3S—C2S	1.566 (9)
C24—C25	1.374 (6)	C1SA—C2S	1.27 (2)
C24—C28	1.523 (5)	C1SB—C2S	1.49 (2)
C25—C26	1.387 (5)		
Bond angles (º)			
N1—C1—C20	126.4 (3)	C32—C33—C37	120.6 (3)
N1—C1—C2	108.9 (3)	C34—C33—C37	121.3 (3)
C20—C1—C2	124.7 (3)	C35—C34—C33	121.7 (3)
C3—C2—C1	107.4 (3)	C34—C35—C30	119.0 (3)
C2—C3—C4	107.8 (3)	C34—C35—C38	119.1 (3)
N1—C4—C5	126.2 (3)	C30—C35—C38	121.9 (3)
N1—C4—C3	108.7 (3)	C40—C39—C44	120.0 (3)
C5—C4—C3	124.7 (3)	C40—C39—C15	119.6 (3)
C4—C5—C6	123.7 (3)	C44—C39—C15	120.4 (3)
C4—C5—C21	118.5 (3)	C41—C40—C39	118.8 (3)
C6—C5—C21	117.8 (3)	C41—C40—C45	120.4 (3)
N2—C6—C5	126.2 (3)	C39—C40—C45	120.8 (3)
N2—C6—C7	108.9 (2)	C42—C41—C40	122.1 (3)
C5—C6—C7	124.6 (3)	C43—C42—C41	117.9 (3)
C8—C7—C6	107.4 (3)	C43—C42—C46	121.6 (3)
C7—C8—C9	107.6 (2)	C41—C42—C46	120.5 (3)
N2—C9—C10	126.0 (3)	C42—C43—C44	122.5 (3)
N2—C9—C8	108.9 (2)	C43—C44—C39	118.6 (3)
C10—C9—C8	125.0 (2)	C43—C44—C47	120.5 (3)

C11—C10—C9	122.9 (2)	C39—C44—C47	120.9 (3)
C11—C10—C30	119.0 (2)	C53—C48—C49	120.0 (2)
C9—C10—C30	118.1 (2)	C53—C48—C20	122.8 (2)
N3—C11—C10	126.3 (3)	C49—C48—C20	117.2 (2)
N3—C11—C12	109.0 (2)	C50—C49—C48	119.2 (3)
C10—C11—C12	124.4 (2)	C50—C49—C54	119.6 (3)
C13—C12—C11	107.6 (3)	C48—C49—C54	121.2 (3)
C12—C13—C14	107.4 (3)	C51—C50—C49	121.7 (3)
N3—C14—C15	125.8 (3)	C50—C51—C52	118.2 (3)
N3—C14—C13	109.1 (2)	C50—C51—C55	120.7 (3)
C15—C14—C13	124.8 (3)	C52—C51—C55	121.0 (3)
C16—C15—C14	123.4 (3)	C51—C52—C53	122.1 (3)
C16—C15—C39	118.3 (2)	C52—C53—C48	118.7 (3)
C14—C15—C39	118.0 (2)	C52—C53—C56	119.2 (2)
N4—C16—C15	126.3 (2)	C48—C53—C56	122.0 (2)
N4—C16—C17	109.2 (2)	F1—Mn1—F2	179.14 (7)
C15—C16—C17	124.1 (3)	F1—Mn1—N3	89.67 (8)
C18—C17—C16	107.3 (3)	F2—Mn1—N3	90.12 (8)
C17—C18—C19	107.5 (2)	F1—Mn1—N2	90.25 (8)
N4—C19—C20	125.9 (3)	F2—Mn1—N2	88.92 (8)
N4—C19—C18	108.8 (2)	N3—Mn1—N2	89.90 (9)
C20—C19—C18	125.2 (2)	F1—Mn1—N1	89.73 (8)
C1—C20—C19	122.9 (3)	F2—Mn1—N1	90.49 (8)
C1—C20—C48	118.1 (3)	N3—Mn1—N1	179.31 (10)
C19—C20—C48	118.9 (2)	N2—Mn1—N1	90.45 (9)
C22—C21—C26	120.3 (3)	F1—Mn1—N4	89.99 (8)
C22—C21—C5	120.4 (3)	F2—Mn1—N4	90.84 (8)
C26—C21—C5	119.3 (3)	N3—Mn1—N4	90.20 (9)
C21—C22—C23	117.9 (4)	N2—Mn1—N4	179.74 (10)
C21—C22—C27	121.2 (3)	N1—Mn1—N4	89.46 (9)
C23—C22—C27	120.9 (3)	C1—N1—C4	107.2 (2)
C24—C23—C22	122.2 (4)	C1—N1—Mn1	126.5 (2)
C25—C24—C23	118.2 (3)	C4—N1—Mn1	126.12 (19)
C25—C24—C28	121.1 (4)	C6—N2—C9	107.2 (2)
C23—C24—C28	120.7 (4)	C6—N2—Mn1	125.98 (19)
C24—C25—C26	122.1 (4)	C9—N2—Mn1	126.84 (19)
C25—C26—C21	119.3 (3)	C11—N3—C14	106.9 (2)
C25—C26—C29	119.2 (3)	C11—N3—Mn1	126.53 (19)

C21—C26—C29	121.5 (3)	C14—N3—Mn1	126.59 (18)
C35—C30—C31	120.1 (3)	C16—N4—C19	107.0 (2)
C35—C30—C10	121.6 (2)	C16—N4—Mn1	126.41 (18)
C31—C30—C10	118.3 (2)	C19—N4—Mn1	126.52 (18)
C32—C31—C30	118.6 (3)	C4S—C3S—C2S	93.0 (9)
C32—C31—C36	120.0 (3)	C1SA—C2S—C3S	151.0 (17)
C30—C31—C36	121.4 (3)	C1SB—C2S—C3S	148.5 (14)
C33—C32—C31	122.3 (3)	C3S—C4S—C5S	94.0 (9)
C32—C33—C34	118.2 (3)		

Supporting Material Figures

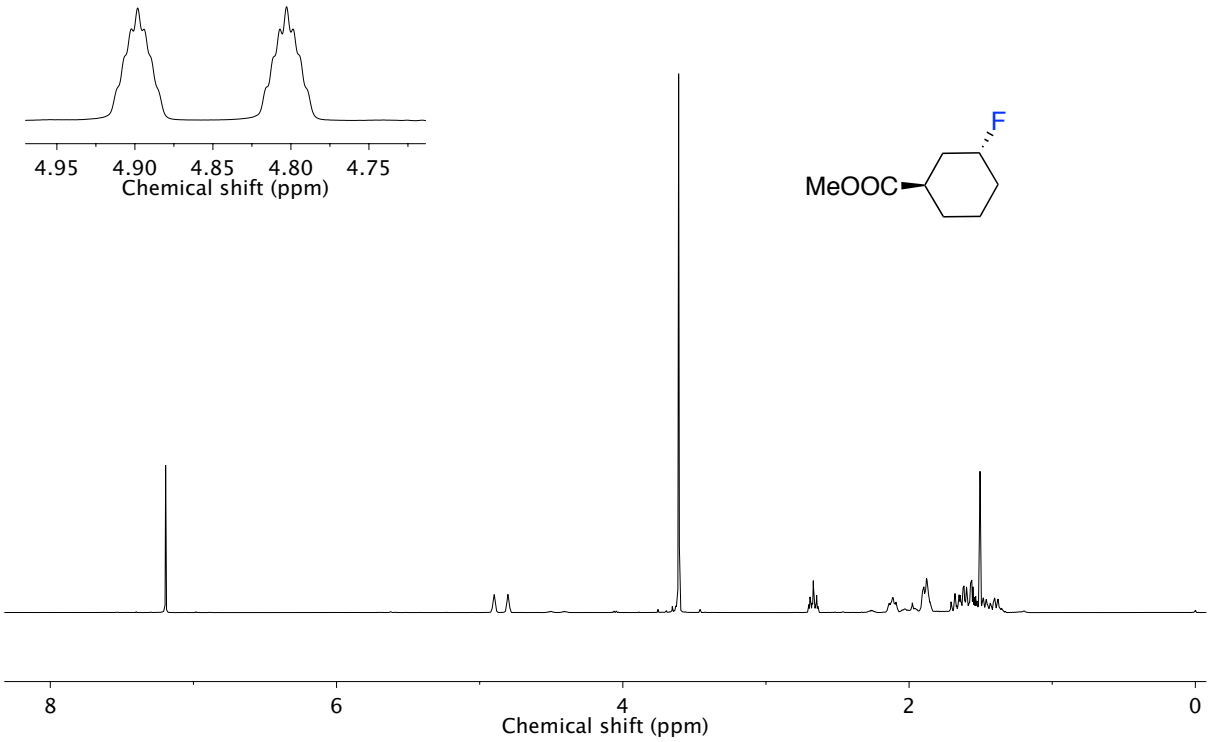

Figure S1. ^{1}HNMR of **compound 8**

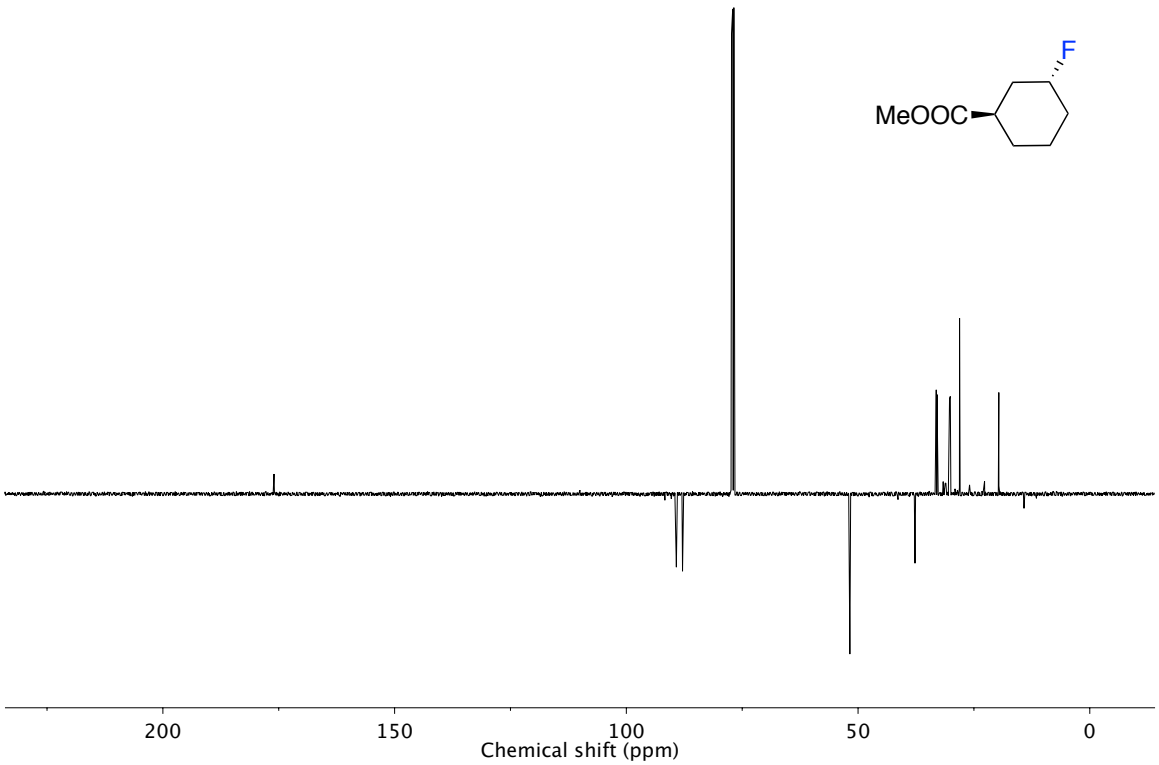

Figure S2. ^{13}C APT NMR spectrum of **compound 8**

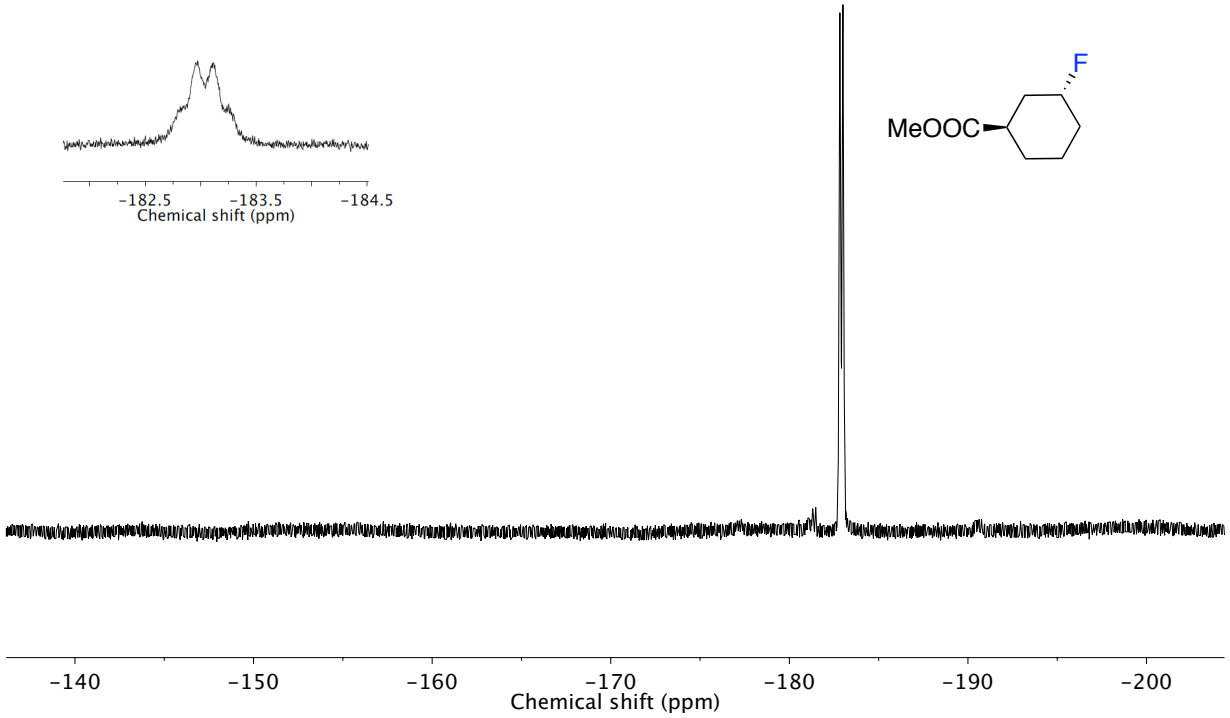

Figure S3. ^{19}F NMR of **compound 8**

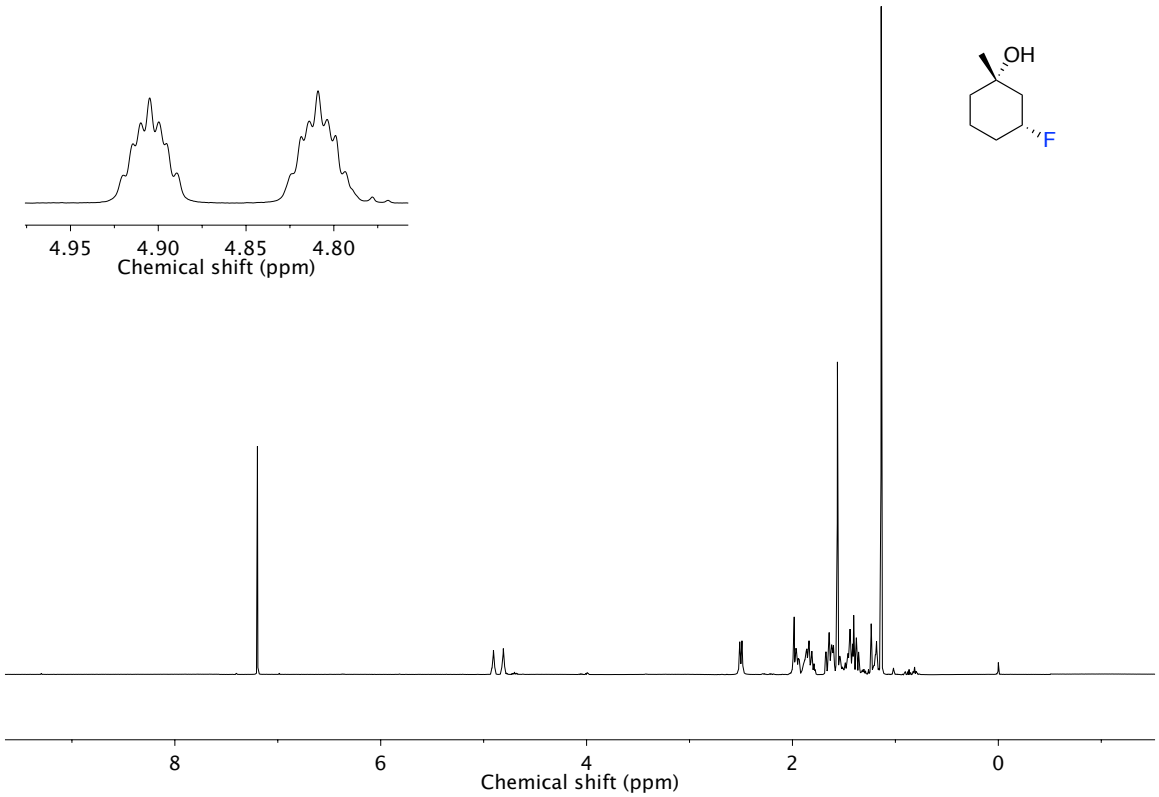

Figure S4. ^{1}HNMR of **compound 9.**

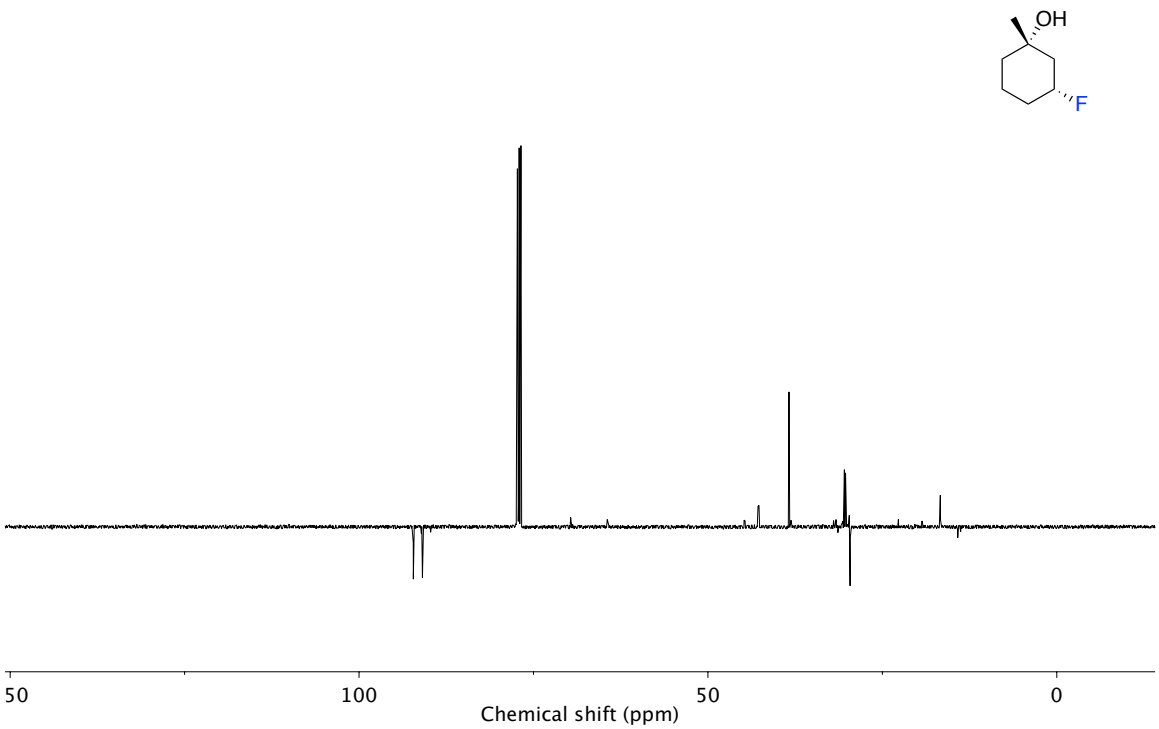

Figure S5. ^{13}C APT NMR spectrum of **compound 9**

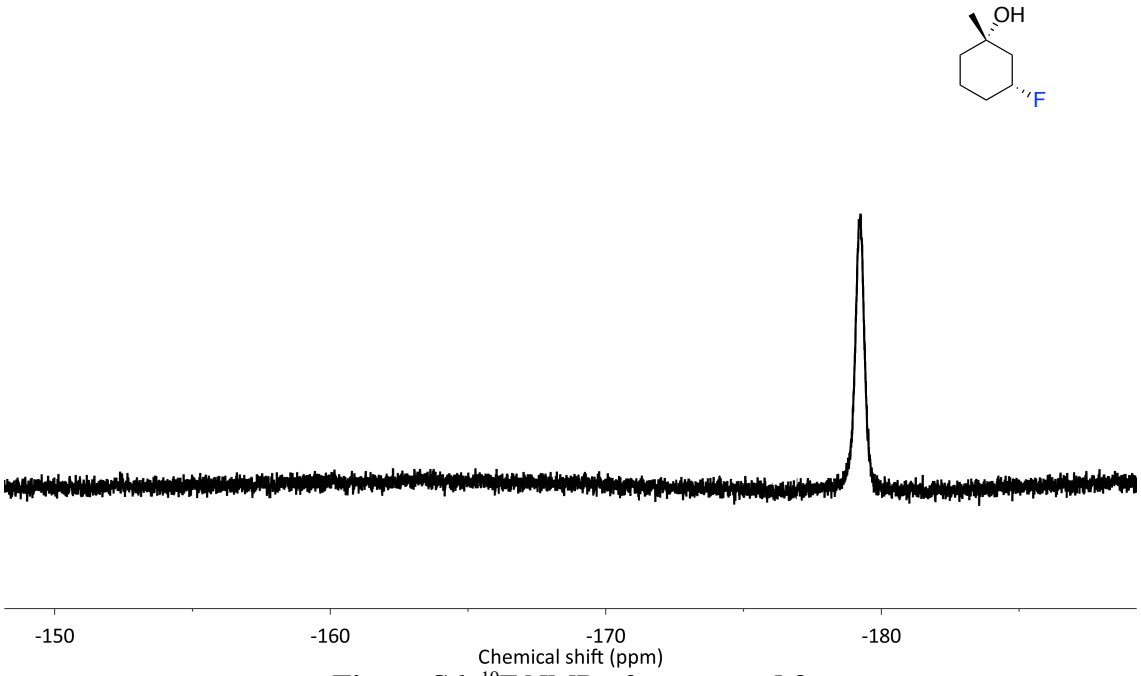

Figure S6. ^{19}F NMR of **compound 9**

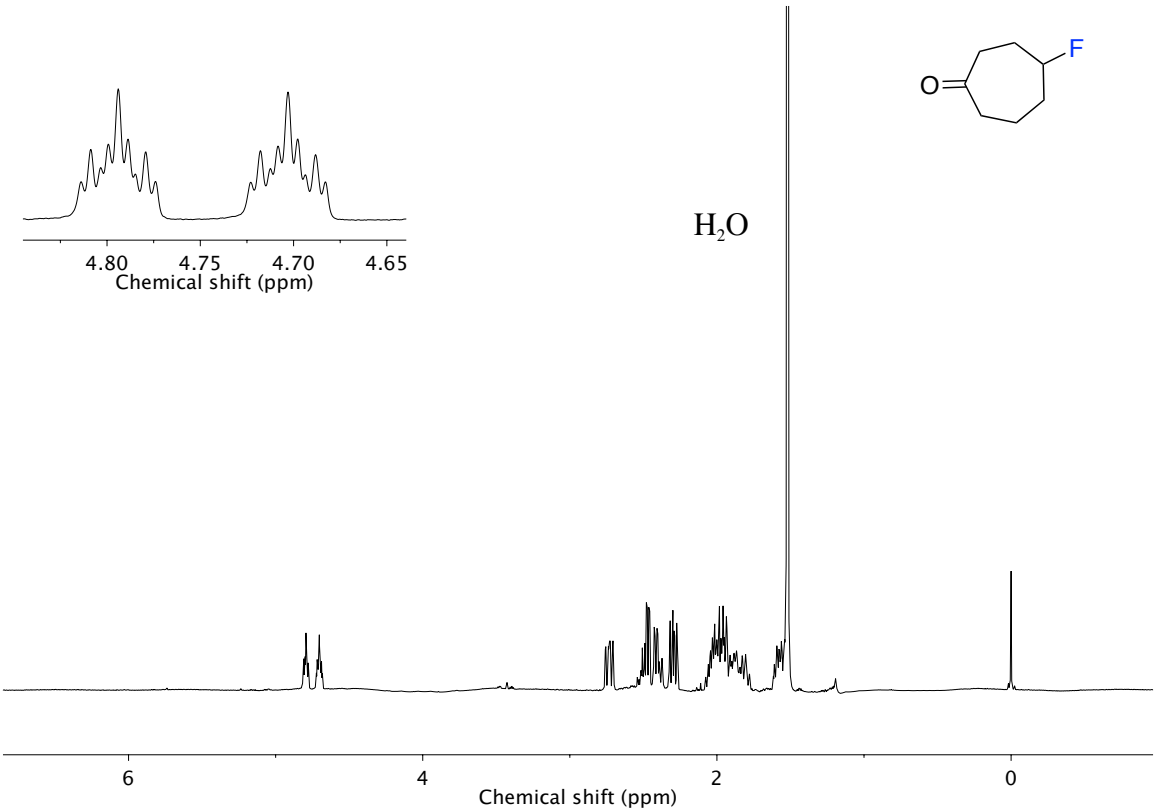

Figure S7. ^{1}H NMR spectrum of **compound 10**.

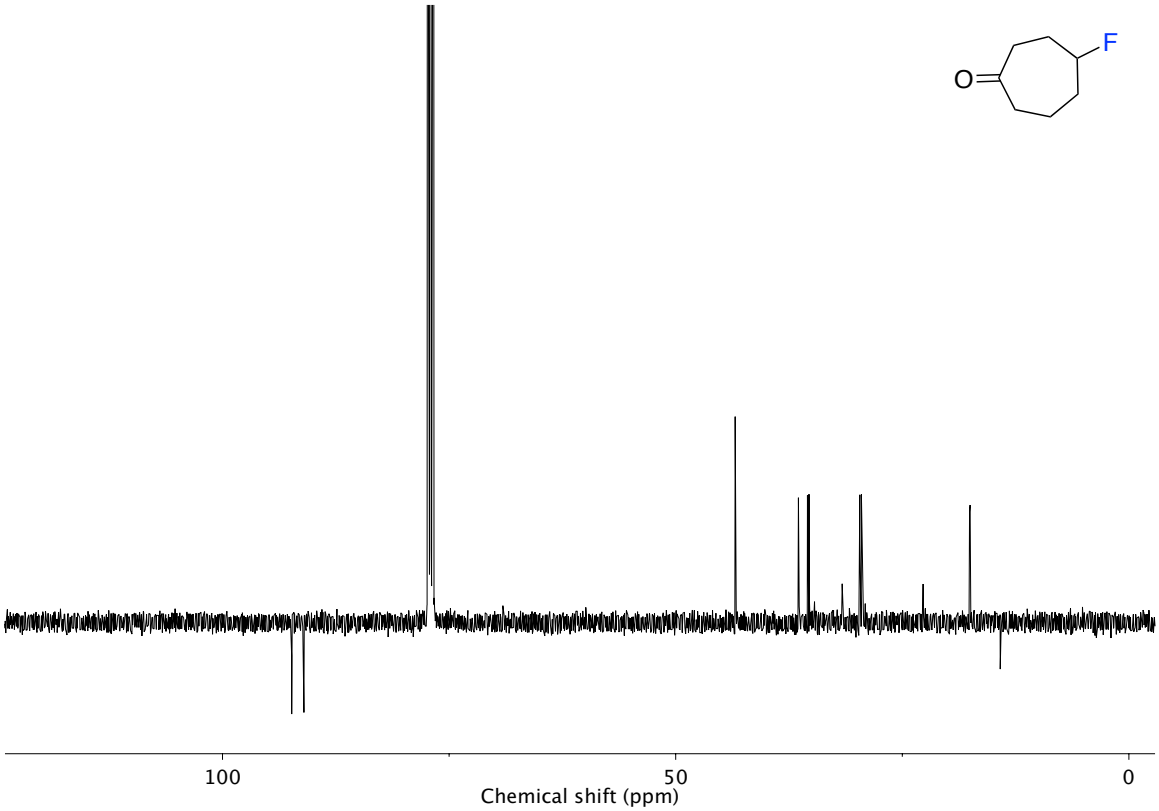

Figure S8. ^{13}C APT NMR spectrum of **compound 10**

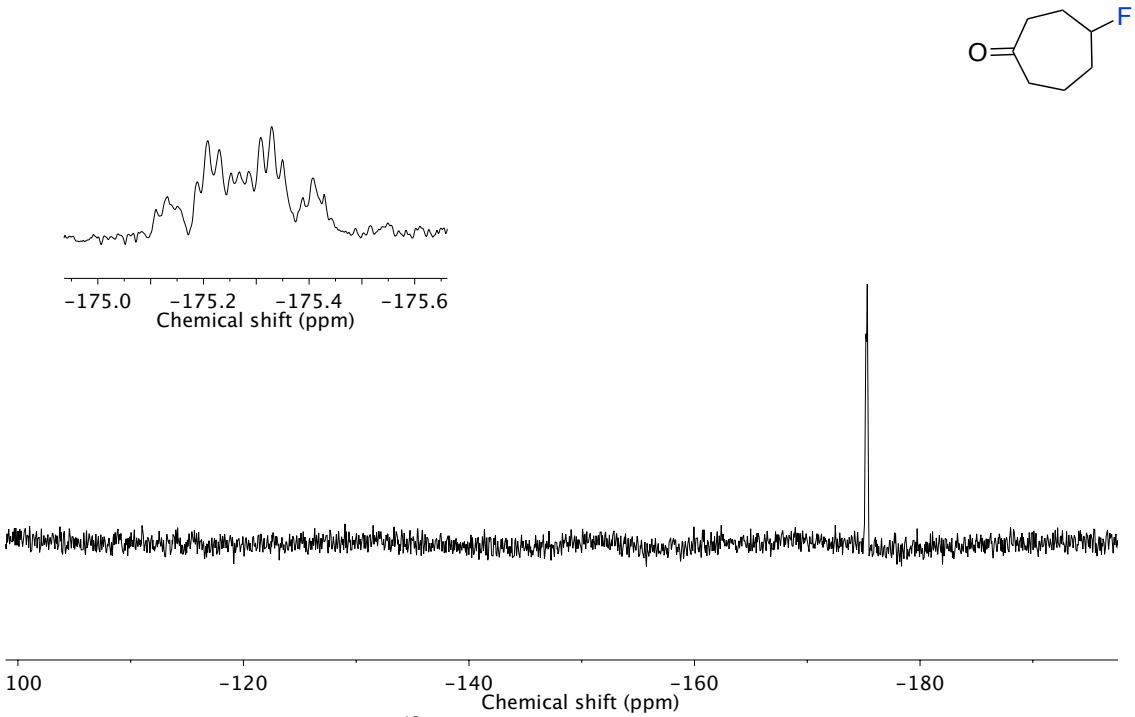

Figure S9. ^{19}F NMR spectrum of **compound 10**

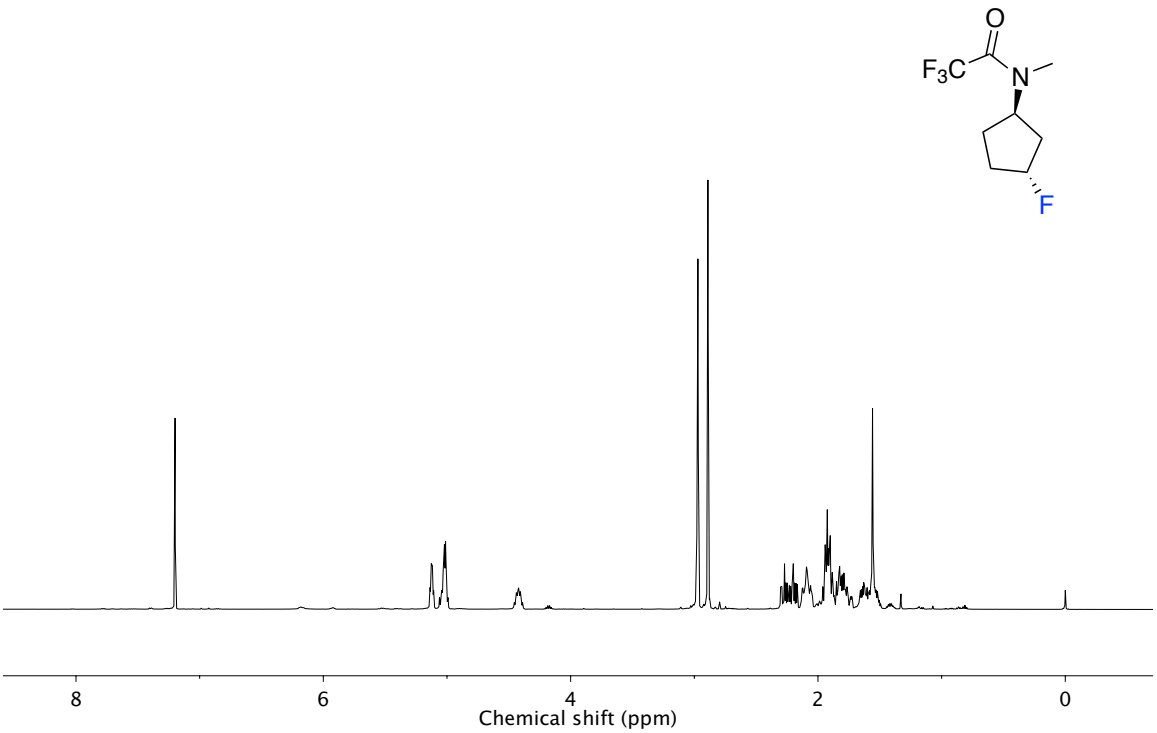

Figure S10. ^{1}H NMR spectrum of *trans*-**11**.

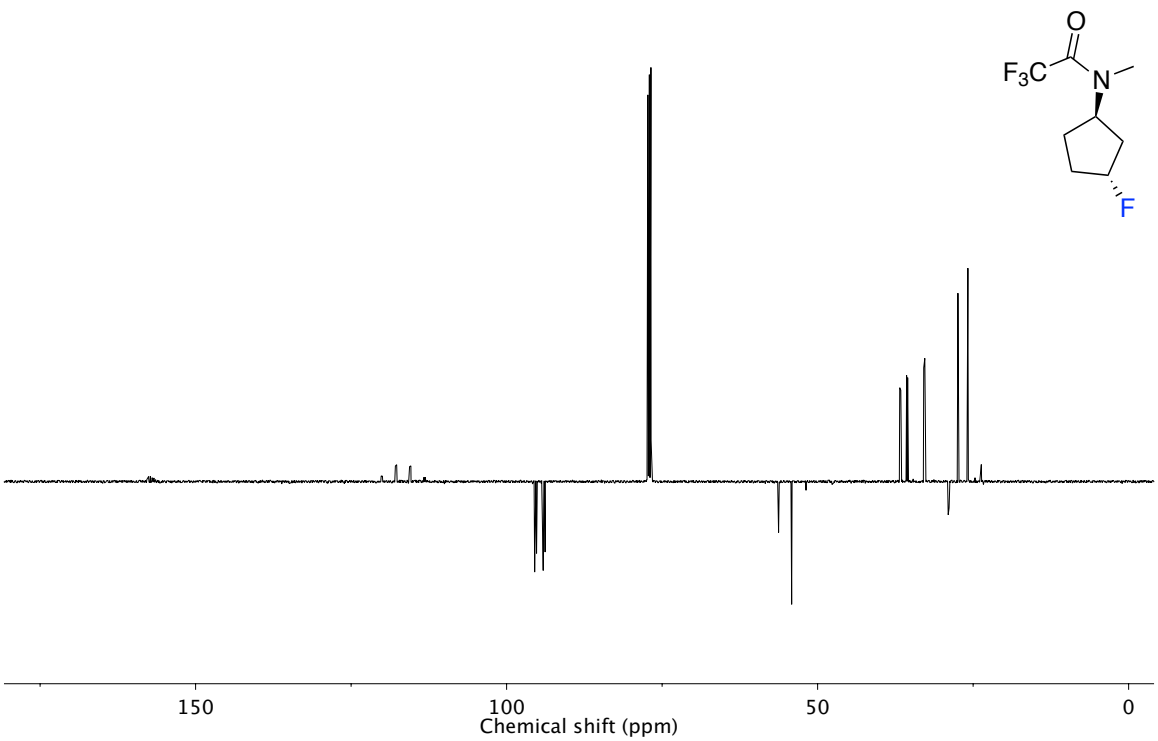

Figure S11. ^{13}C APT NMR spectrum of *trans*-**11**.

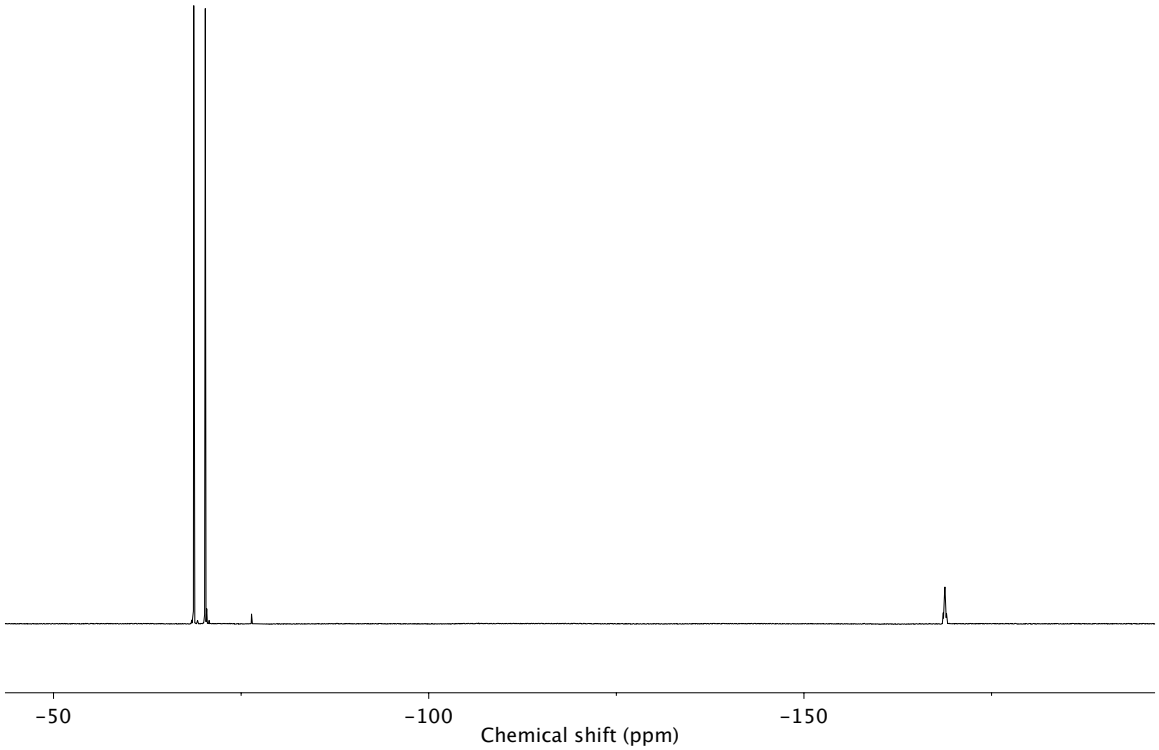

Figure S12. ^{19}F NMR spectrum of *cis*- and *trans*-**11**.

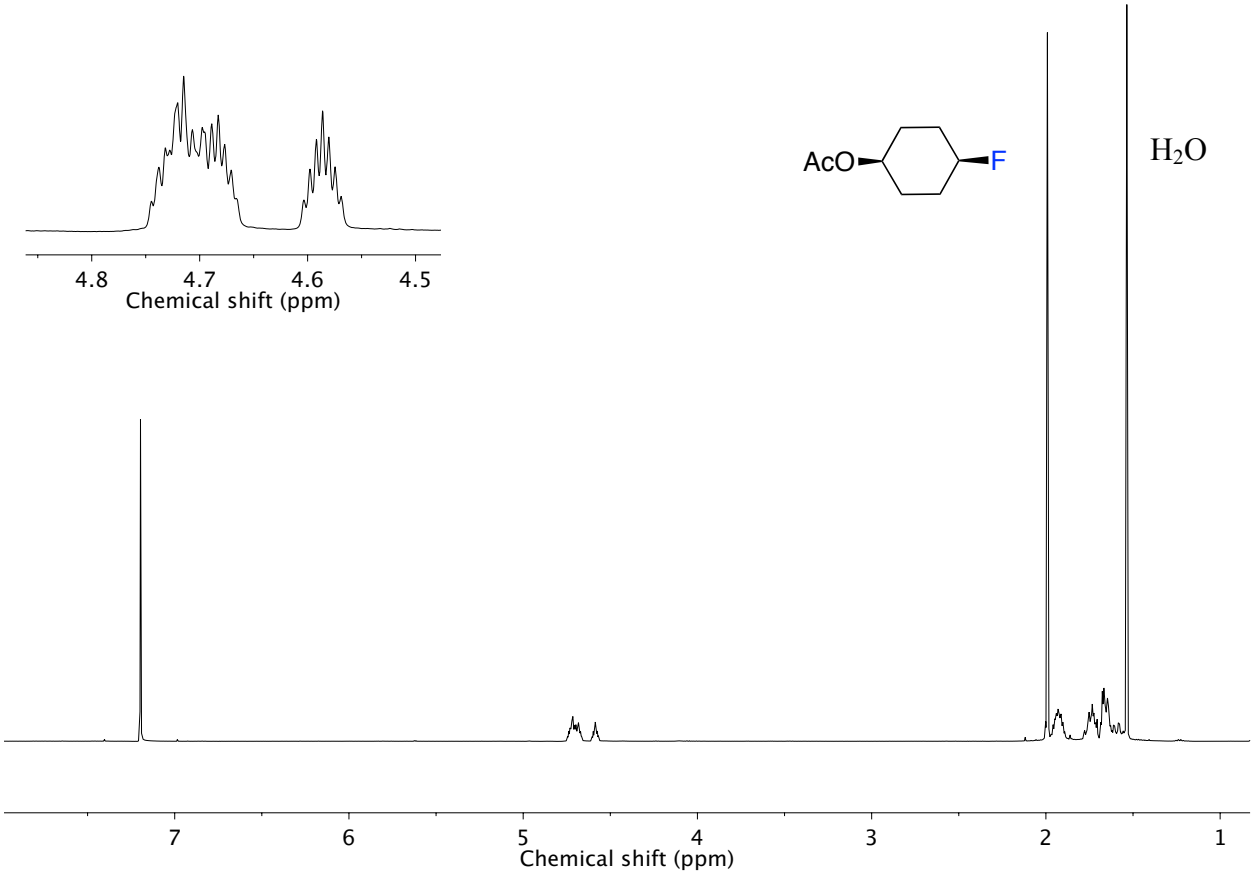

Figure S13. ^{1}H NMR spectrum of **compound 12a** (cis)

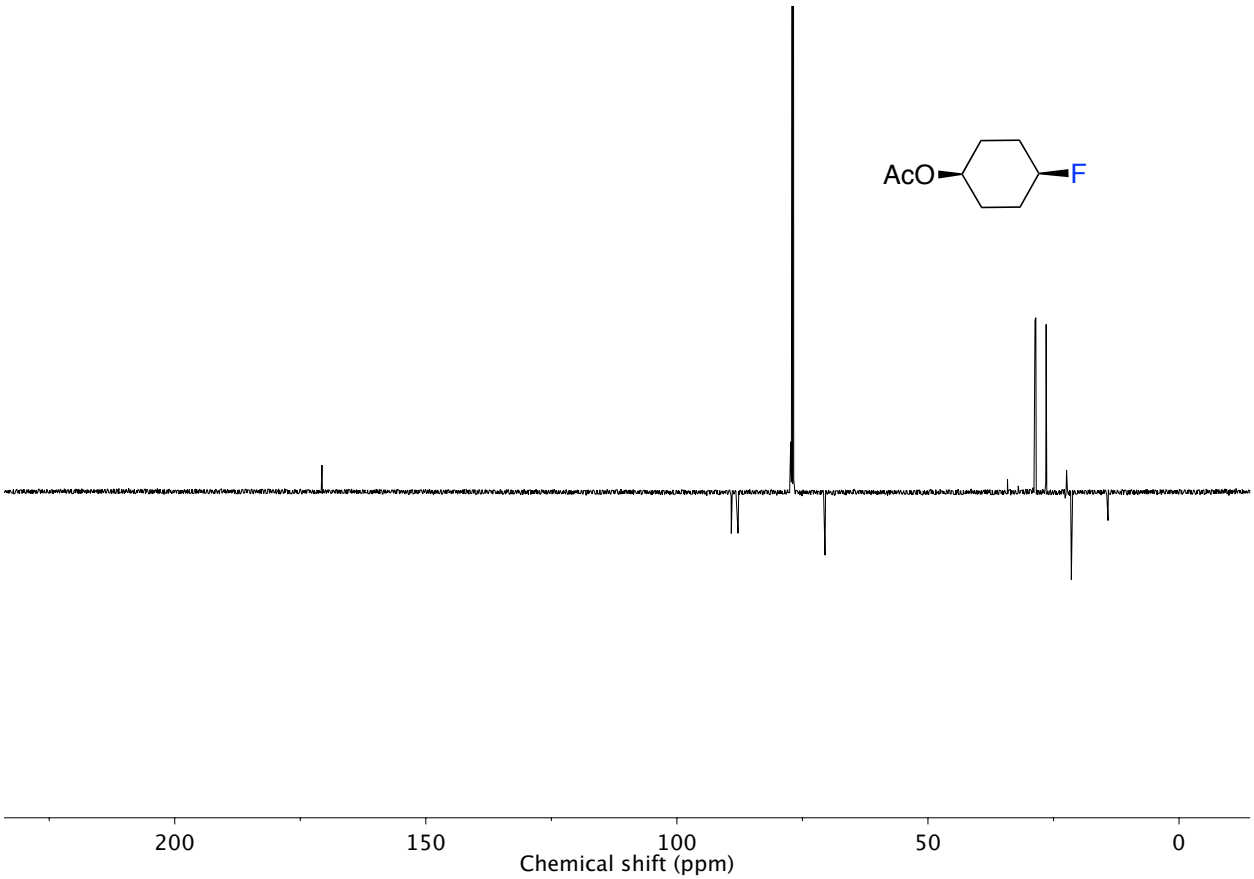

Figure S14. ^{13}C APT NMR spectrum of **compound 12a** (cis)

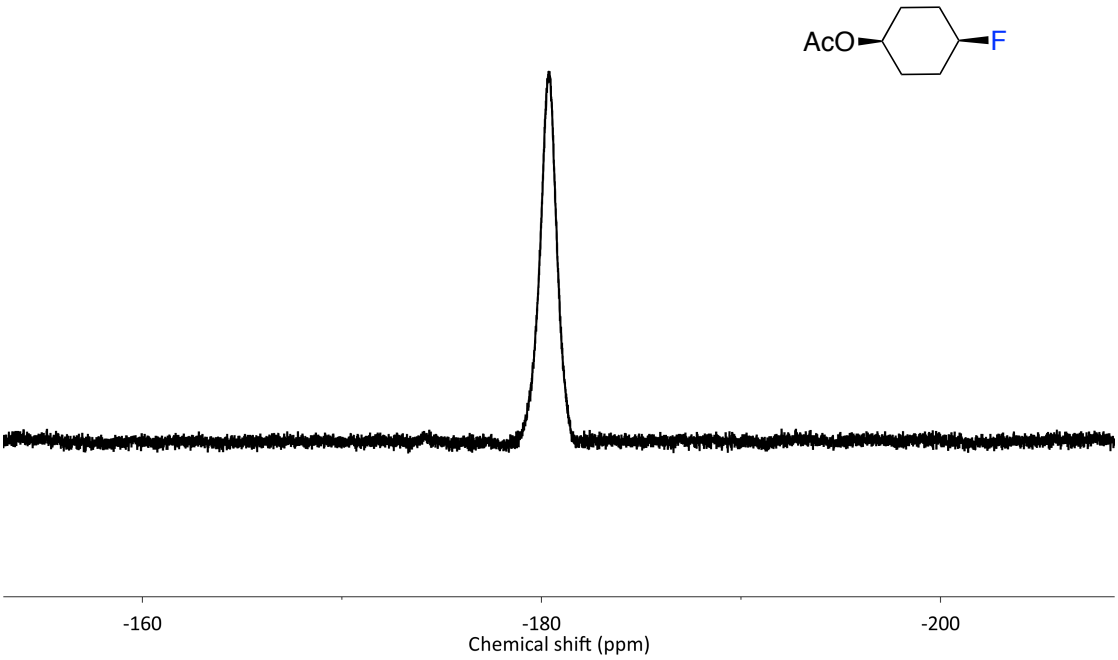

Figure S15. ^{19}F NMR spectrum of **compound 12a** (cis).

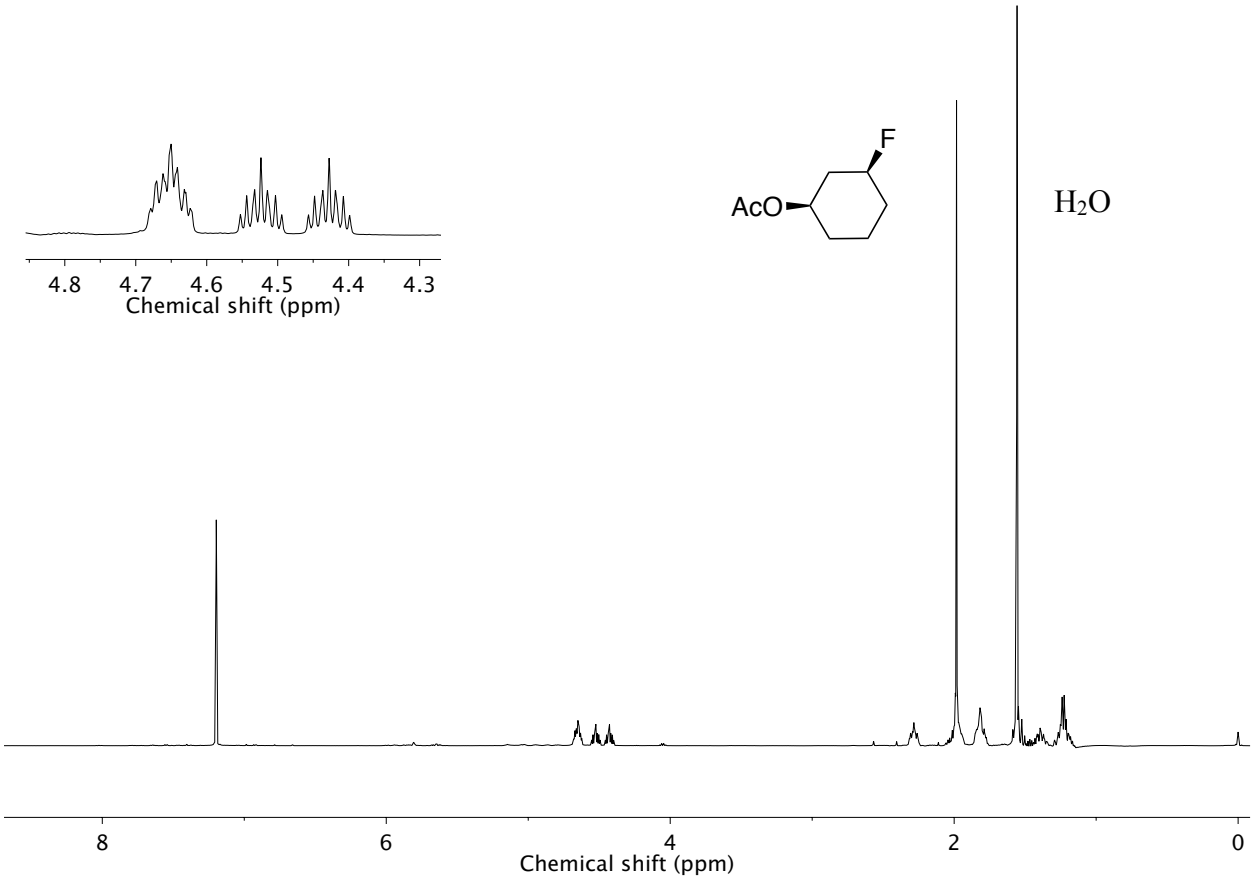

Figure S16. ^{1}H NMR spectrum of **compound 12b** (cis).

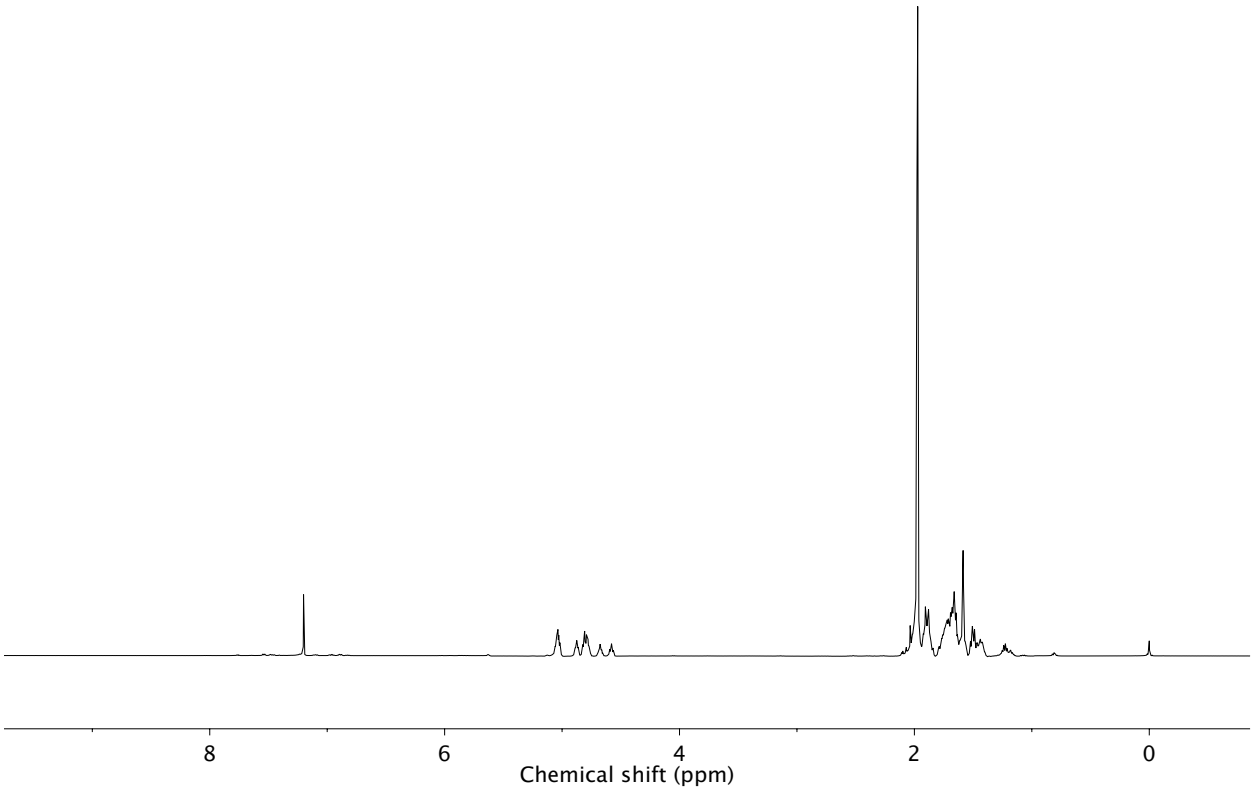

Figure S17. ^{1}H NMR spectrum of **compound 12a** (trans)+**12b** (trans)

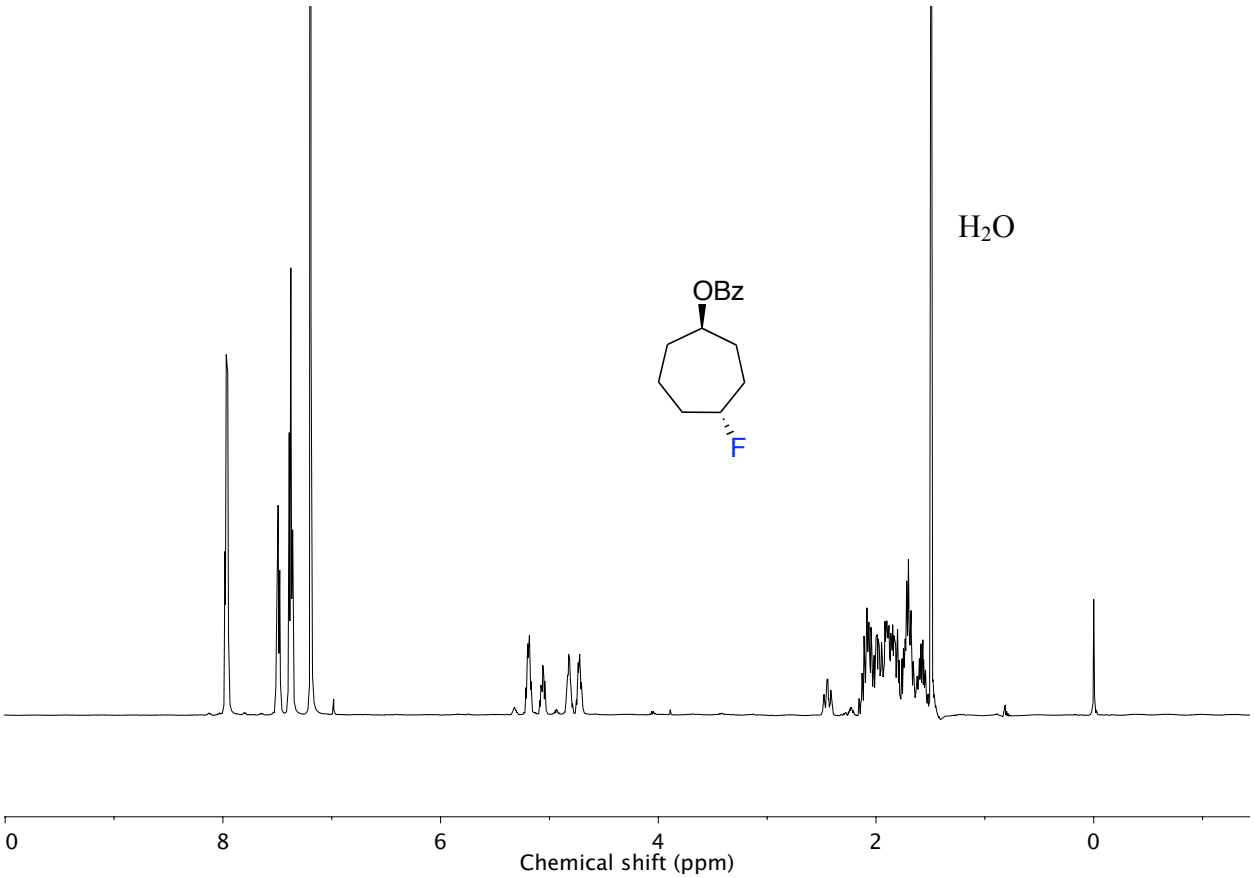

Figure S18. ^{1}H NMR spectrum of **compound 13.**

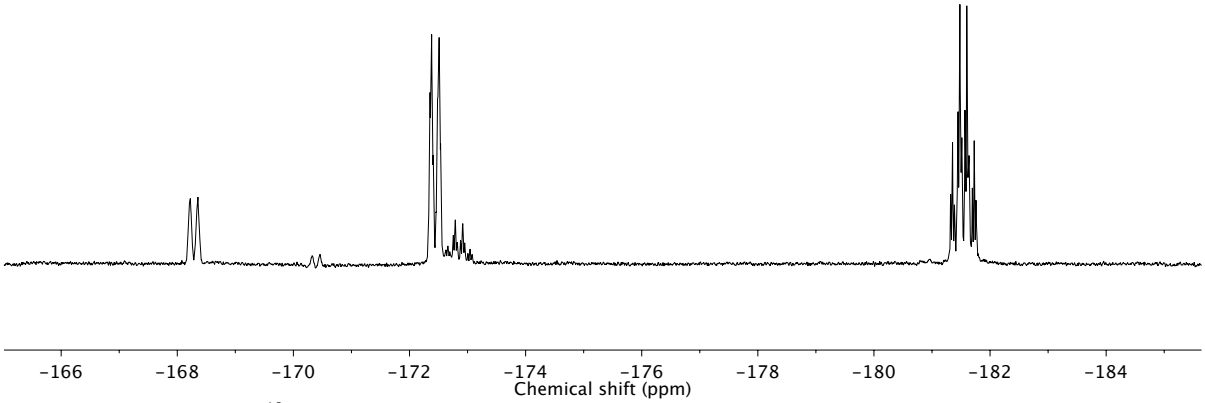

Figure S19. ^{19}F NMR spectrum of 5α-androstan-17-one fluorination products.

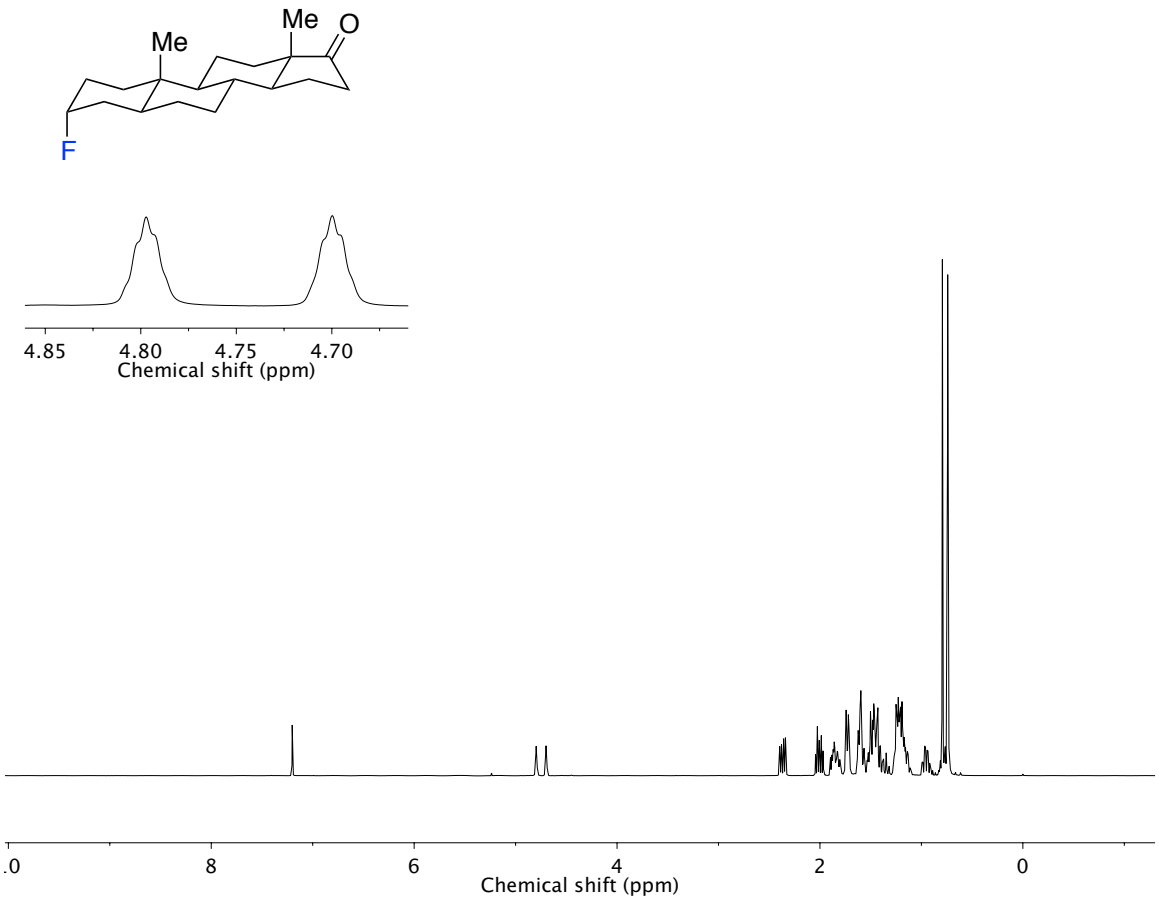

Figure S20. [1]HNMR spectrum of 3α-fluoro-5α-androstan-17-one

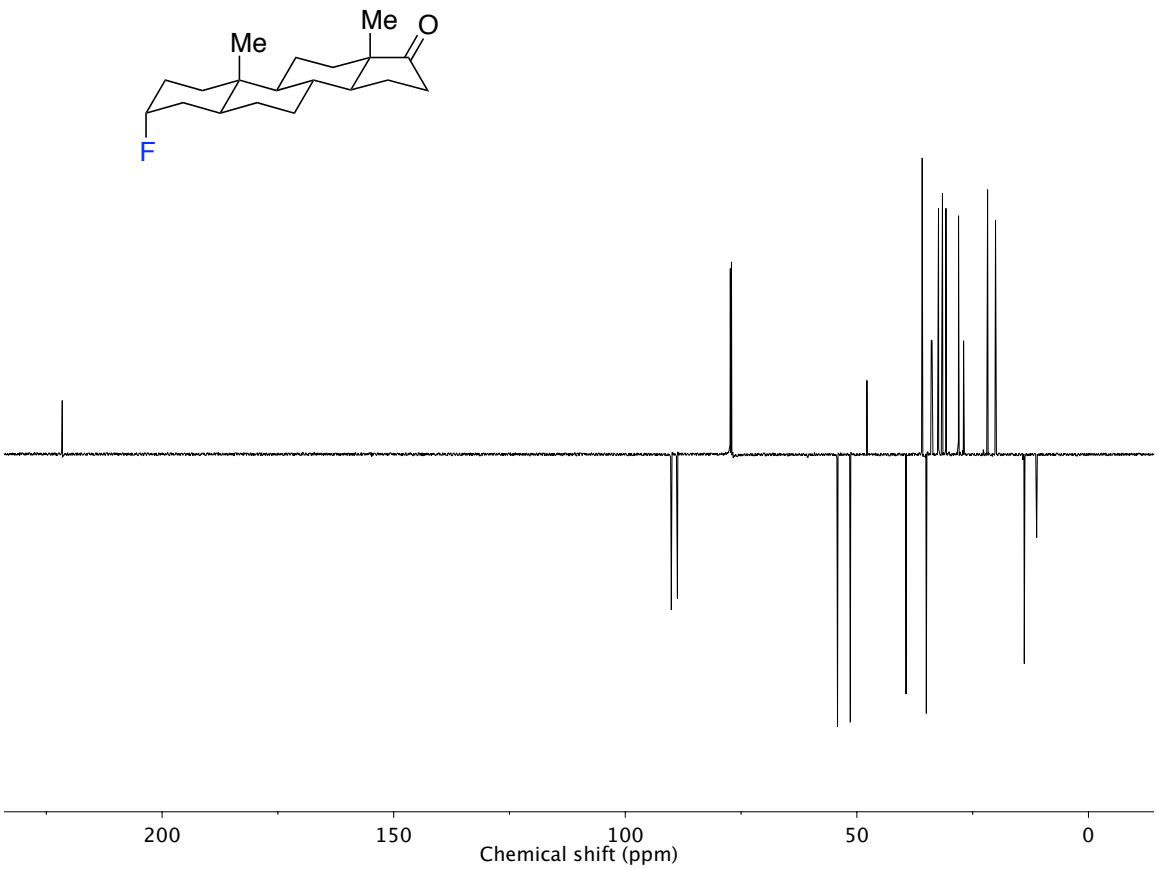

Figure S21. ^{13}C APT NMR spectrum of 3α-fluoro-5α-androstan-17-one.

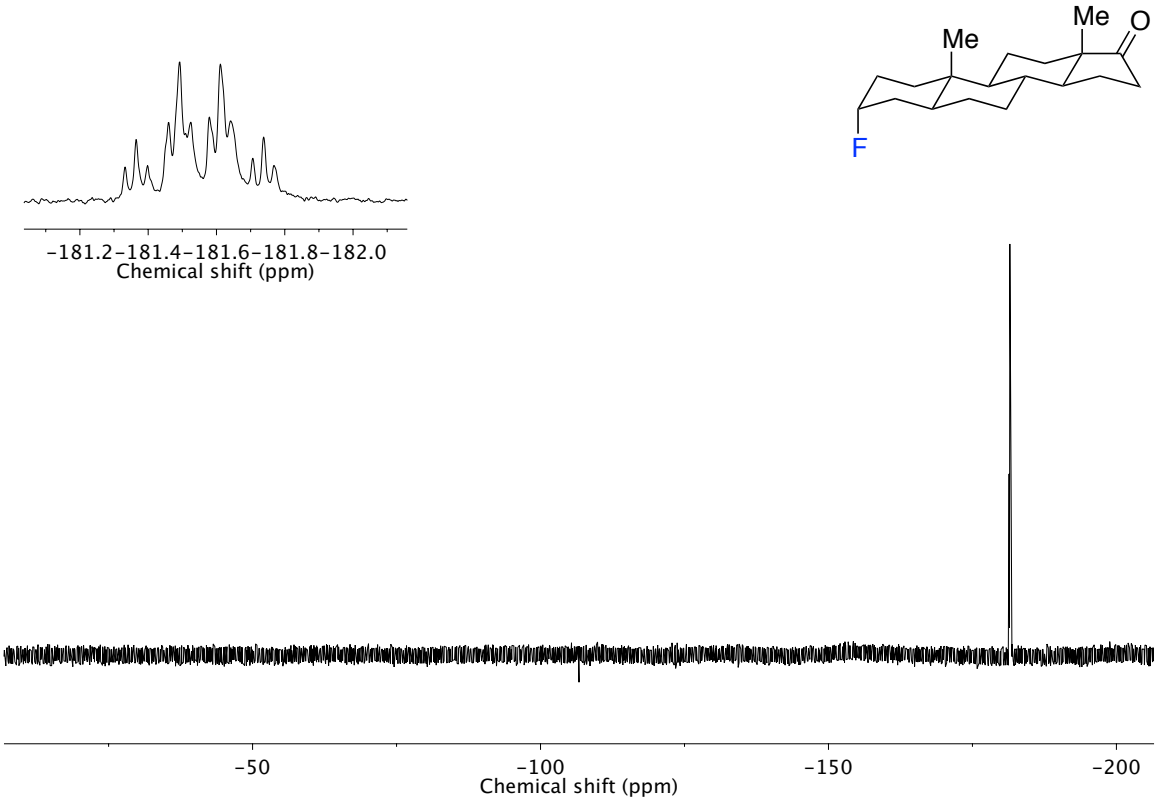

Figure S22. ^{19}F NMR spectrum of 3α-fluoro-5α-androstan-17-one.

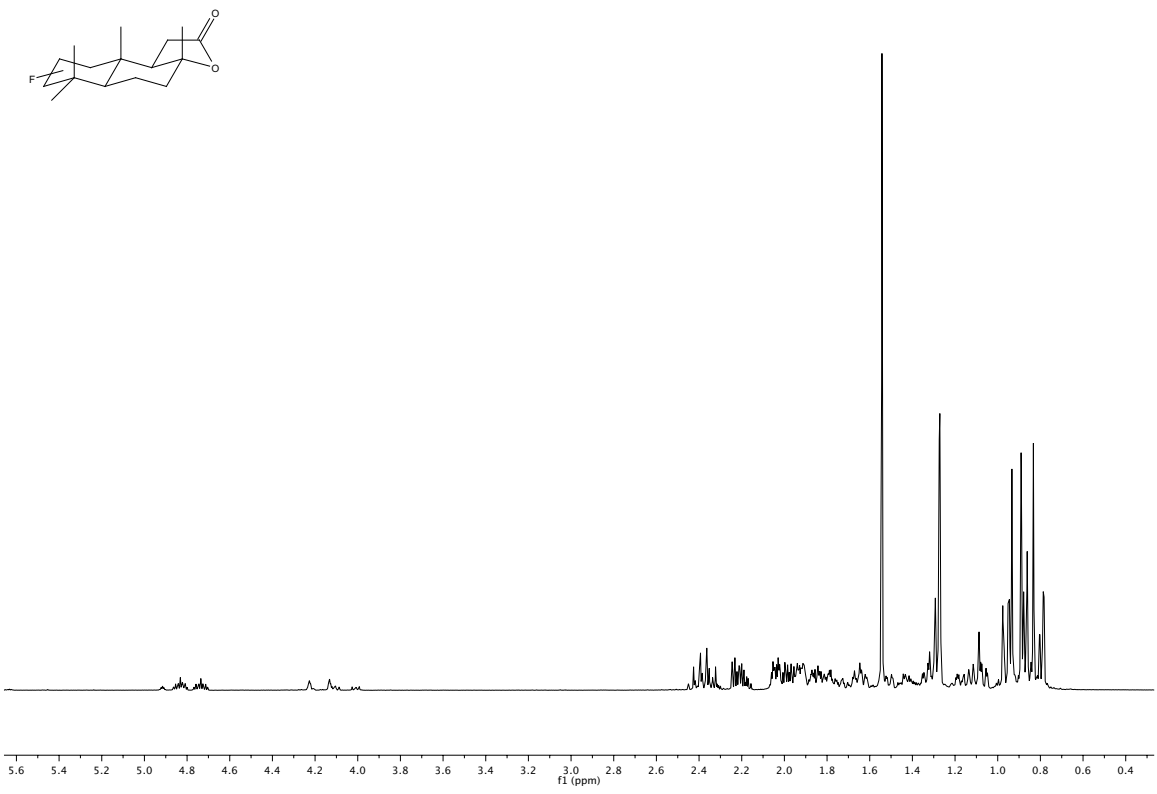

Figure S23. ^{1}H NMR spectrum of sclareolide fluorination products

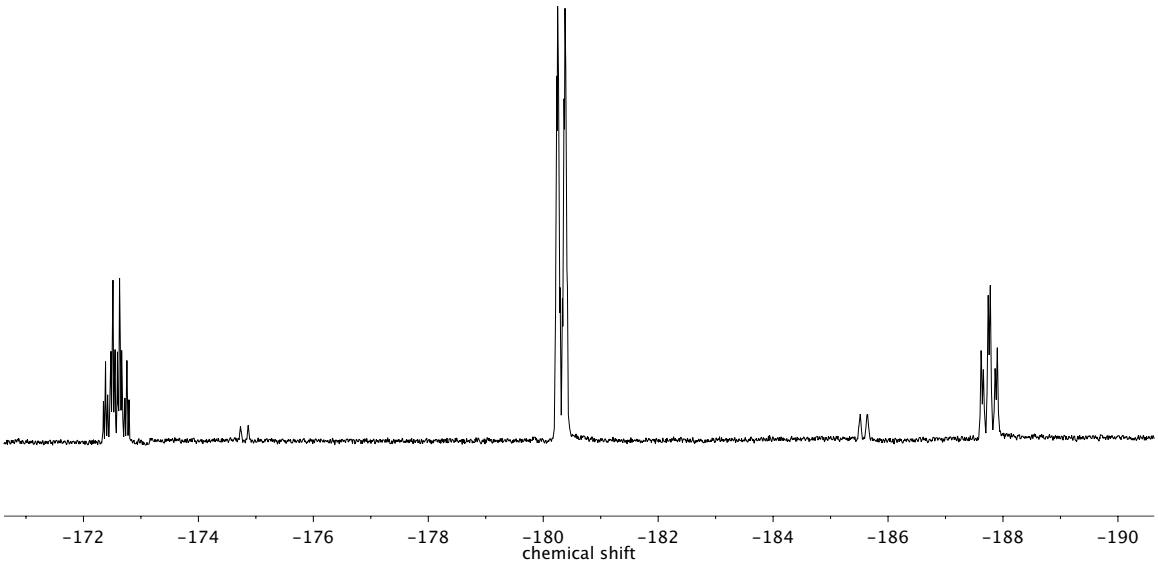

Figure S24. ^{19}F NMR spectrum of sclareolide fluorination products.

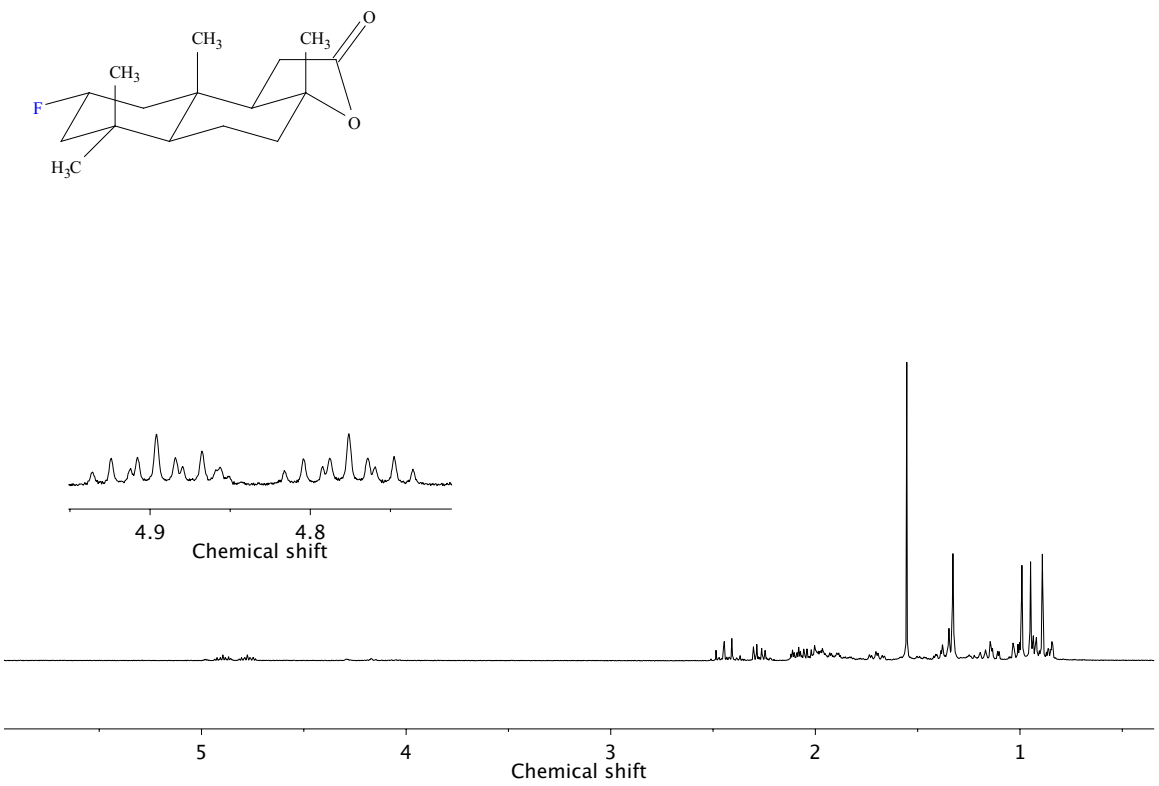

Figure S25. ^{1}H NMR spectrum of 2α-fluoro-sclareolide

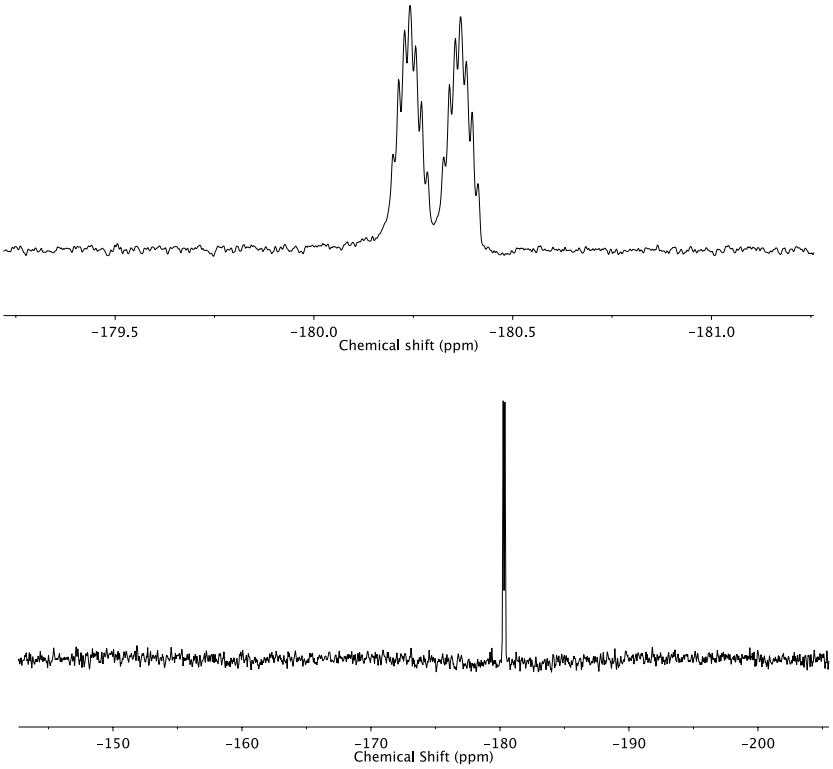

Figure S26. ^{19}F NMR spectrum of 2α-fluoro-sclareolide

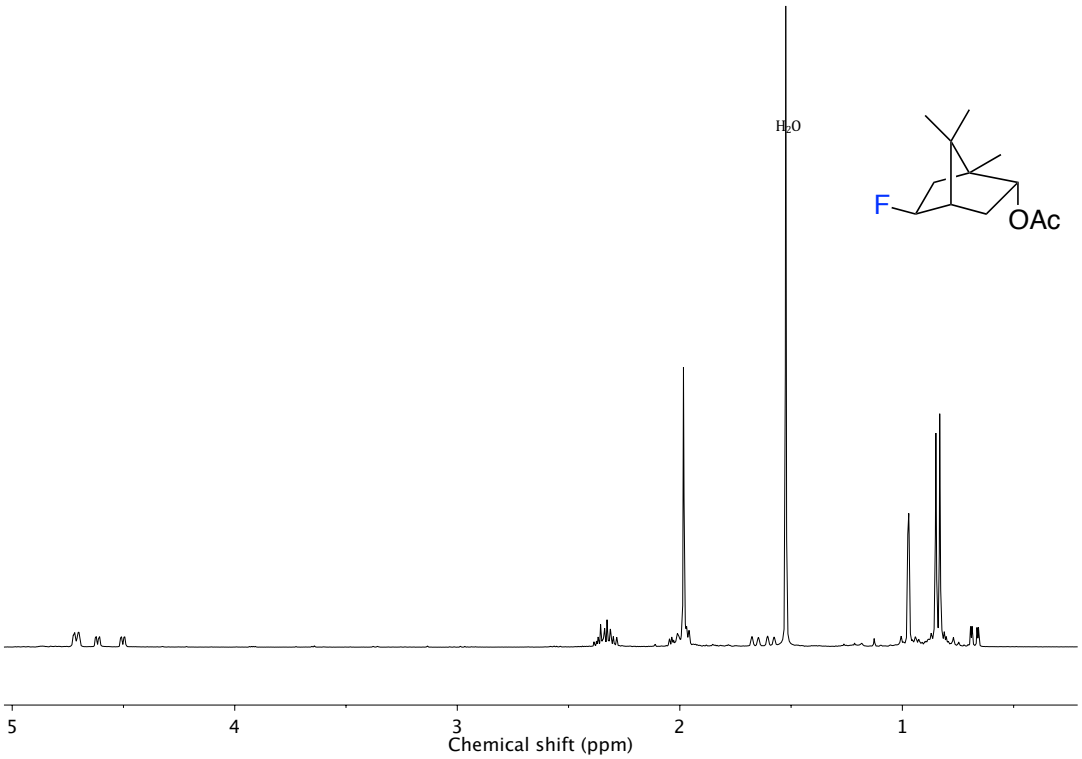

Figure S27. ^{1}H NMR spectrum of *exo*-5-fluoro-bornyl acetate.

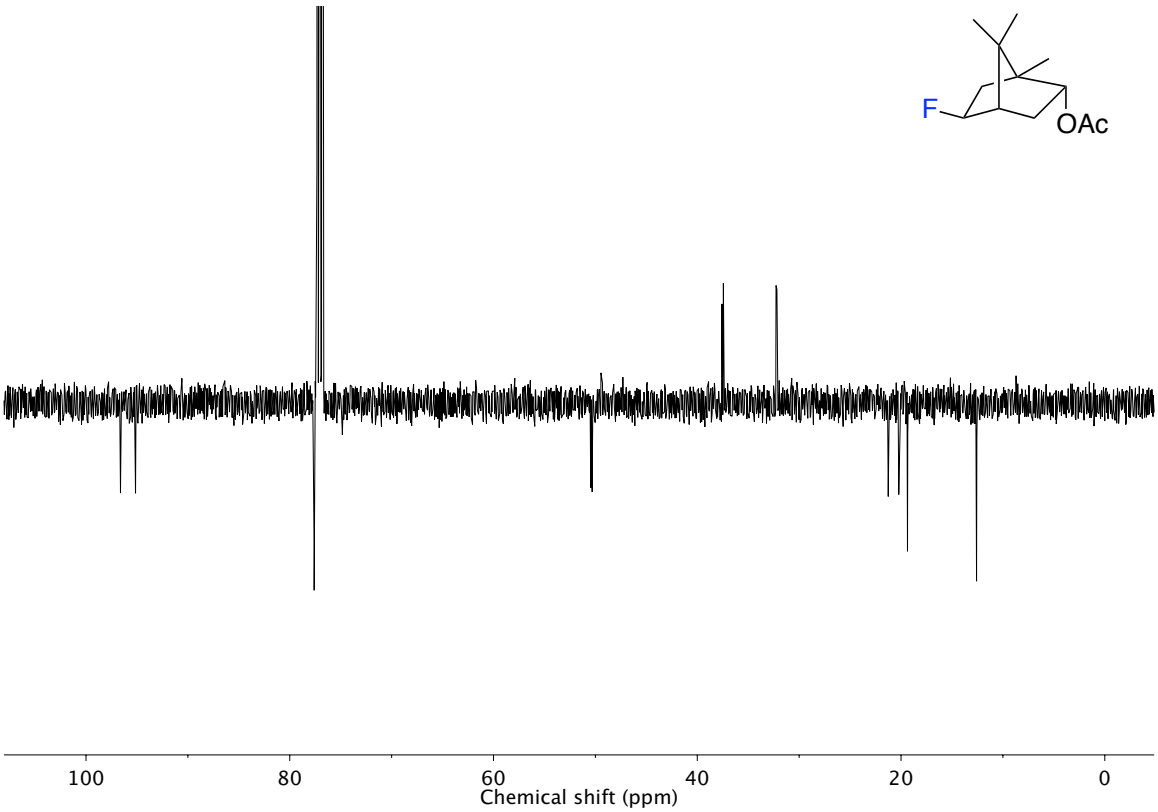

Figure S28. ^{13}C APT NMR spectrum of *exo*-5-fluoro-bornyl acetate.

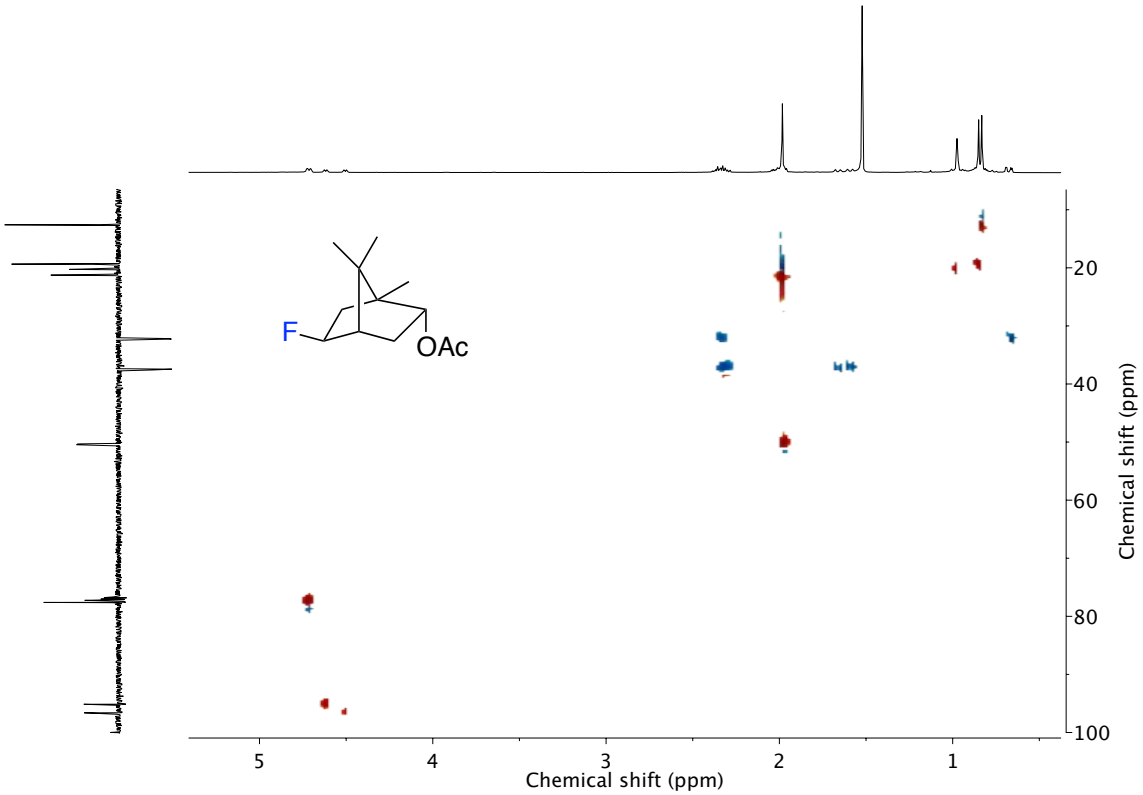

Figure S29a. C-H COSY NMR spectrum of *exo*-5-fluoro-bornyl acetate.

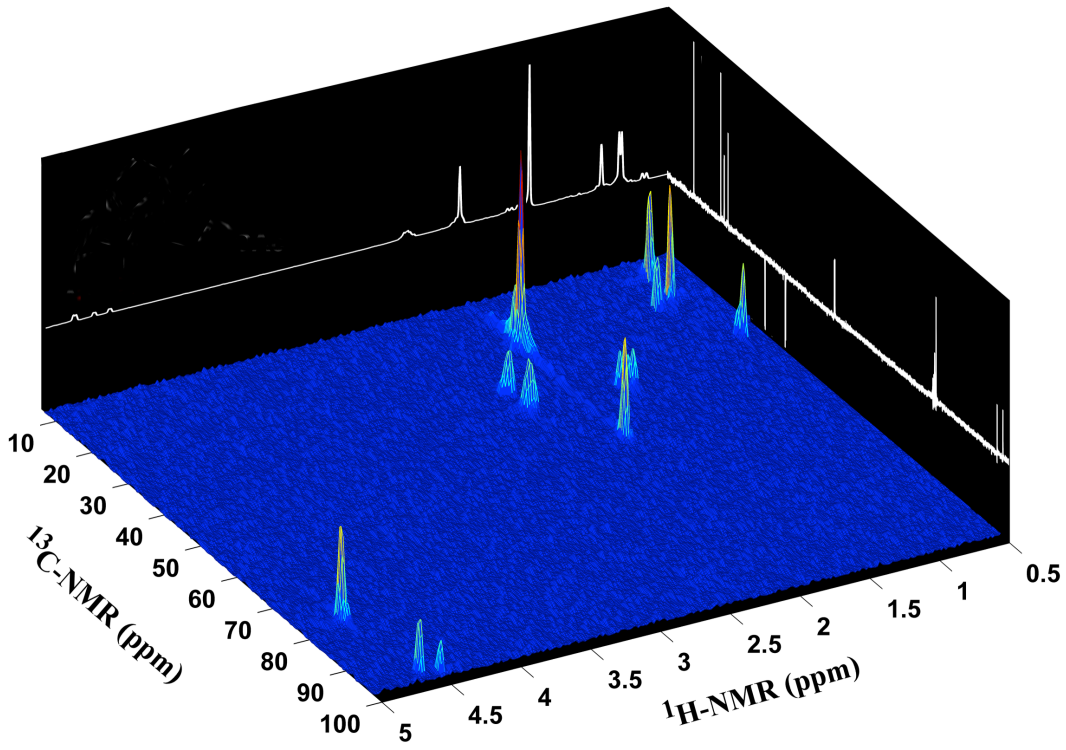

Figure 29b. ^{1}H-^{13}C HSQC NMR spectroscopy of exo-5-fluoro-bornyl acetate. The ^{1}H-NMR splitting pattern of the proton at d 4.55 (ddd) indicates that the fluorination occurred at a secondary carbon position adjacent to a methylene group. The ^{13}C NMR spectrum displays a doublet for the C4 carbon with a coupling constant of 16 Hz, consistent with a 2J ^{13}C-F coupling, which, together with the ^{1}H NMR data, clearly designates C5 as the fluorination position. The *exo*-fluorine configuration was confirmed by the ^{19}F-NMR signal at -158 ppm, whereas the endo product would have a signal at -190 ppm (cf. reference 37).

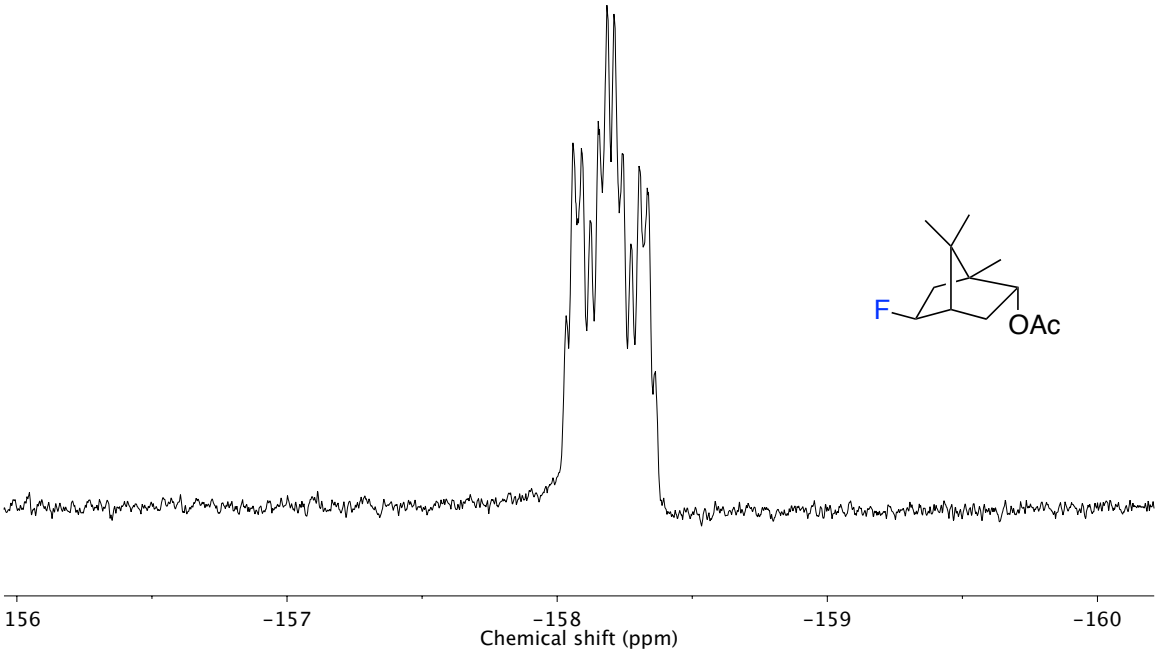

Figure S30. ^{19}F NMR spectrum of *exo*-5-fluoro-bornyl acetate.

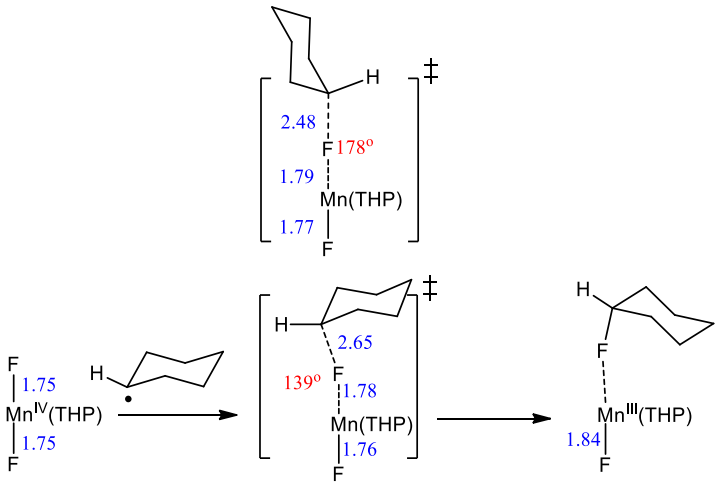

Figure S31. Computed geometrical parameters for the equatorial and axial F-transfer transition states.

Table S6. Cartesian coordinates of B3LYP/LACVP** optimizations:

(1) X = F, axial fluorination transition state

F1	0.4679462437	-0.3340580408	2.2353409992
Mn2	0.3549780341	-0.1206310253	3.9999500259
N3	-1.4436843299	0.8426893741	3.7242496700
N4	1.3254526804	1.6466115326	3.8361473633
N5	2.1439012704	-1.0835914316	4.2336876306
N6	-0.6207232201	-1.8891589919	4.1358803532
C7	-0.6060984501	3.1314029050	3.4741327270
C8	3.6399042023	0.8543301795	4.1045895327
C9	1.3118065647	-3.3789937804	4.4548295081
C10	-2.9344907025	-1.0977127947	3.8436103056
C11	0.7505363629	2.8747544063	3.6306239499
C12	2.6805019674	1.8416832224	3.9171329951
C13	3.3836509229	-0.5034139444	4.2447174014
C14	2.3242003900	-2.4298775124	4.4027793278
C15	-0.0478019770	-3.1192060805	4.3328672489
C16	-1.9766698211	-2.0816334759	4.0564726768
C17	-2.6794934249	0.2583980677	3.6808220686
C18	-1.6200050298	2.1817981255	3.5101673709
C19	-3.0253353663	2.4583775083	3.3259370617
C20	-3.6808075483	1.2690599101	3.4322743912
H21	-3.4407891154	3.4401085480	3.1393100961
H22	-4.7426812600	1.0769498124	3.3497401673
C23	-2.2696403602	-3.4854301206	4.2129328315
C24	-1.0799327590	-4.1254026924	4.3832980365
H25	-3.2646625568	-3.9102843679	4.1906146829
H26	-0.8991965519	-5.1823119317	4.5293042013
C27	2.9715488112	3.2454983759	3.7609513065
C28	1.7812831722	3.8822209577	3.5839476125
H29	3.9658293680	3.6718590562	3.7830599026
H30	1.5993078816	4.9375475326	3.4309842355
C31	3.7343473390	-2.7135501613	4.5238104528
C32	4.3888803979	-1.5232728534	4.4267177890
H33	4.1528388733	-3.7015728476	4.6645242330
H34	5.4537803963	-1.3360235506	4.4715228899
H35	1.6064701583	-4.4128104605	4.5999723836
H36	4.6768946953	1.1718314438	4.1393146695
H37	-0.8966075057	4.1628511400	3.3055557072
H38	-3.9694612577	-1.4190684000	3.7940117095
C39	-0.6584791401	-1.4105867872	-0.4718095495
C40	-0.4548852873	1.1770991449	-0.3894349363
C41	0.8579987619	-1.4870127869	-0.7485834428
H42	-1.1959914936	-1.5870131629	-1.4253235350

H43	-0.9683666620	-2.2200038443	0.1996061810
C44	1.0570825900	1.0325506385	-0.6660670917
H45	-0.9523258036	1.4946905248	-1.3290115011
H46	-0.6387737100	1.9814040227	0.3326148363
C47	1.3568822261	-0.2332350390	-1.4828568278
H48	1.0840745968	-2.3911028850	-1.3268016724
H49	1.3767154389	-1.5681952519	0.2127273321
H50	1.4271896970	1.9259410948	-1.1846588196
H51	1.5755466949	0.9678240279	0.2970922919
H52	2.4344415161	-0.3118297264	-1.6744882031
H53	0.8695486787	-0.1623624943	-2.4678612241
C54	-1.0723964122	-0.0930414083	0.0903355361
H55	-1.9241999743	-0.0469994173	0.7609446081
F56	0.2147853666	0.1017617386	5.7411611896

(2) X = F, equatorial fluorination transition state

F1	0.1159640120	-0.1199469700	2.1741146720
Mn2	0.1879448988	-0.0373663366	3.9640085680
N3	-1.6607439244	0.8070955812	3.9824744791
N4	1.0314364459	1.8053925262	3.8349513352
N5	2.0368862476	-0.8835631979	3.9235265165
N6	-0.6548318713	-1.8819240249	4.0733078416
C7	-1.0100371704	3.1714434291	3.8493762514
C8	3.3995546234	1.1542130411	3.7801133252
C9	1.3873946281	-3.2470333406	4.0709866064
C10	-3.0229050630	-1.2312046122	4.1302617343
C11	0.3674143529	3.0039314655	3.8065698144
C12	2.3714076443	2.0868557037	3.7735444845
C13	3.2348421437	-0.2222858064	3.8520609191
C14	2.3202382261	-2.2227220879	3.9848463894
C15	0.0100026480	-3.0795821630	4.1118385247
C16	-1.9945632174	-2.1637240491	4.1382141401
C17	-2.8586332841	0.1455804582	4.0586802832
C18	-1.9434775503	2.1469177382	3.9311954762
C19	-3.3722512988	2.3389420402	3.9747590082
C20	-3.9375349182	1.1027515758	4.0530936821
H21	-3.8627716466	3.3031673542	3.9488361016
H22	-4.9871129049	0.8444391675	4.1048383143
C23	-2.1825900533	-3.5913847518	4.2185493285
C24	-0.9443795858	-4.1571045044	4.2026436027
H25	-3.1457454988	-4.0807281833	4.2805157834
H26	-0.6824659425	-5.2060492237	4.2487996145
C27	2.5603241369	3.5148598090	3.7023755355
C28	1.3225308435	4.0813831340	3.7227995918
H29	3.5240517141	4.0037298864	3.6454108933
H30	1.0616420373	5.1309185305	3.6858664067

C31	3.7493796685	-2.4147349476	3.9485984966
C32	4.3144595198	-1.1788114740	3.8665920249
H33	4.2400683606	-3.3785771148	3.9844571028
H34	5.3642374496	-0.9200382230	3.8213946618
H35	1.7662009524	-4.2626070634	4.1122056944
H36	4.4152464347	1.5323013970	3.7285173308
H37	-1.3883205112	4.1875235202	3.8178823439
H38	-4.0382577970	-1.6093854943	4.1870462963
F39	0.2576193728	0.0439300535	5.7347096515
C40	-0.0823366929	-0.1901453835	-0.2983404080
C41	-1.4046860087	-0.8766819721	-0.3839165169
C42	-0.0430160659	1.2774396096	-0.5666402761
H43	0.8323454470	-0.7599674778	-0.1990769771
C44	-2.1212997049	-0.5309177881	-1.7152153159
H45	-2.0403292105	-0.5345768217	0.4497214828
H46	-1.2992446467	-1.9611342979	-0.2711123947
C47	-0.7640068499	1.6142347005	-1.8979690517
H48	-0.5622362229	1.8050631048	0.2507985146
H49	0.9855236443	1.6539125096	-0.5774381510
C50	-2.1679441137	0.9890566442	-1.9424963010
H51	-3.1355387869	-0.9501707575	-1.7143101916
H52	-1.5833376856	-1.0049415255	-2.5479957732
H53	-0.8240455335	2.7025045284	-2.0267756024
H54	-0.1691963048	1.2282292266	-2.7375136505
H55	-2.6496947211	1.2121027188	-2.9030422658
H56	-2.7932404007	1.4510649300	-1.1642900616

(3) X = OH, axial fluorination transition state

F1	0.6011665062	-0.3427718588	2.2387901071
Mn2	0.4076005919	-0.1217474564	4.0134894191
N3	-1.3773179462	0.8471145631	3.7209038272
N4	1.3967797671	1.6463952905	3.8555859851
N5	2.1832513932	-1.0902443974	4.3139834200
N6	-0.5743045447	-1.9026630428	4.0840918789
C7	-0.5278882057	3.1356466160	3.4963404746
C8	3.6962156075	0.8405882689	4.1716509455
C9	1.3475488582	-3.3979159970	4.4151497373
C10	-2.8778922110	-1.0905294169	3.7890721273
C11	0.8286774301	2.8754890107	3.6525501723
C12	2.7488421778	1.8357703964	3.9600414376
C13	3.4296745812	-0.5159569619	4.3181339957
C14	2.3607122947	-2.4464295631	4.4275133867
C15	-0.0090991264	-3.1377124483	4.2575568868
C16	-1.9276687611	-2.0872994968	3.9785243901
C17	-2.6157776587	0.2693543189	3.6671297557
C18	-1.5466667480	2.1899955203	3.5272740745

C19	-2.9513788407	2.4768668494	3.3500521554
C20	-3.6127556106	1.2892662392	3.4377748197
H21	-3.3625674323	3.4633673514	3.1790771025
H22	-4.6757051187	1.1039732206	3.3511408732
C23	-2.2287313646	-3.4963327109	4.0806145803
C24	-1.0443494169	-4.1448112654	4.2520828456
H25	-3.2240014140	-3.9176986301	4.0221121391
H26	-0.8688426410	-5.2064923627	4.3649473334
C27	3.0495922296	3.2402240906	3.8092484355
C28	1.8643500787	3.8814258423	3.6189192275
H29	4.0450669276	3.6628469861	3.8452321217
H30	1.6879969475	4.9378338603	3.4661863759
C31	3.7683015922	-2.7353930620	4.5429743905
C32	4.4276270365	-1.5441526759	4.4760367263
H33	4.1853265843	-3.7280552898	4.6525944720
H34	5.4935992021	-1.3642278708	4.5191453725
H35	1.6420001536	-4.4361059830	4.5277652721
H36	4.7362282669	1.1478510336	4.2121555785
H37	-0.8162170040	4.1690779072	3.3346176677
H38	-3.9144770103	-1.4042049925	3.7198674896
O39	0.1898042598	0.1137547732	5.8000236861
H40	0.9204812144	-0.3106547751	6.2730950980
C41	-0.5196427073	-1.5823919911	-0.3555301923
C42	-0.4978687909	1.0252434665	-0.3491904130
C43	0.9781697990	-1.5525189031	-0.7249865477
H44	-1.0977331052	-1.8646070608	-1.2582499185
H45	-0.7157803286	-2.3719568290	0.3803166900
C46	1.0012723408	0.9712394679	-0.7089723185
H47	-1.0651593928	1.3171663827	-1.2558804247
H48	-0.6872420456	1.8171299861	0.3859702571
C49	1.3349063259	-0.2885837315	-1.5209707117
H50	1.2380965991	-2.4552681732	-1.2912604639
H51	1.5600326188	-1.5637285168	0.2034347197
H52	1.2828626252	1.8764969195	-1.2606868951
H53	1.5774208770	0.9571759207	0.2227959242
H54	2.3991759505	-0.2969195856	-1.7878576431
H55	0.7760105317	-0.2767295593	-2.4698226626
C56	-1.0187158784	-0.2756380149	0.1621050628
H57	-1.8575800745	-0.2710522342	0.8505116712

(4) X = OH, equatorial fluorination transition state

F1	0.0624506772	-0.0489455966	2.2155775525
Mn2	0.1739430671	-0.0127380422	4.0157472552
N3	-1.6437157601	0.8789198634	4.1174068229
N4	1.0684955656	1.8073740720	3.8749124608
N5	2.0068679494	-0.9119874388	3.9043490696

N6	-0.7108558493	-1.8417182233	4.0654094845
C7	-0.9329037851	3.2255472777	3.9927619798
C8	3.4124992129	1.0935692901	3.6999220989
C9	1.2892730199	-3.2622551958	3.9335762263
C10	-3.0553671707	-1.1273778594	4.2159867078
C11	0.4373718148	3.0221633240	3.8990918108
C12	2.4112067874	2.0539994202	3.7637940508
C13	3.2163722904	-0.2808494968	3.7482161430
C14	2.2506555694	-2.2625350272	3.8550587533
C15	-0.0806699920	-3.0576757449	4.0351922795
C16	-2.0542134149	-2.0879662156	4.1635879309
C17	-2.8564186733	0.2466658606	4.1855463010
C18	-1.8917042457	2.2253484058	4.0846726419
C19	-3.3150660836	2.4535962953	4.1421841297
C20	-3.9109749865	1.2308546172	4.2041927613
H21	-3.7820421565	3.4297636250	4.1284372348
H22	-4.9665304561	0.9984510359	4.2518775706
C23	-2.2827096703	-3.5131575009	4.1922286518
C24	-1.0636485404	-4.1123905043	4.1134250773
H25	-3.2580077572	-3.9768085341	4.2616850838
H26	-0.8315651987	-5.1693560512	4.1045425111
C27	2.6369645886	3.4793301966	3.7126651517
C28	1.4174538688	4.0771191677	3.7961527932
H29	3.6101045192	3.9438520517	3.6213583442
H30	1.1829063556	5.1335072697	3.7874140487
C31	3.6639490642	-2.4901067107	3.6904982733
C32	4.2599807413	-1.2663717583	3.6246091994
H33	4.1255005933	-3.4667647915	3.6248362531
H34	5.3089741602	-1.0360024083	3.4939671554
H35	1.6372198395	-4.2895538699	3.8993458743
H36	4.4329913815	1.4461459994	3.5910048435
H37	-1.2847212757	4.2520244248	3.9845186851
H38	-4.0796760939	-1.4801054670	4.2780009365
O39	0.2832880671	0.0305945152	5.8388479091
H40	1.1316398712	-0.3347820435	6.1286245586
C41	0.1057973697	-0.1258346063	-0.2279987410
C42	-1.1227597671	-0.9401423589	-0.4531340887
C43	0.0099722015	1.3331929271	-0.5206454963
H44	1.0655865242	-0.5992001449	-0.0625698911
C45	-1.6341589455	-0.7364077502	-1.9029187604
H46	-1.9106065831	-0.6073756132	0.2427538952
H47	-0.9490552394	-2.0015870061	-0.2467083351
C48	-0.4936531145	1.5503826584	-1.9716656907
H49	-0.7146497342	1.7944344537	0.1708537123
H50	0.9659931131	1.8426646481	-0.3597256660
C51	-1.7864729273	0.7583769533	-2.2337134388

H52	-2.5902005911	-1.2572532968	-2.0448813451
H53	-0.9181192046	-1.1926145698	-2.6004587621
H54	-0.6567922489	2.6194374723	-2.1610474665
H55	0.2851377659	1.2189779552	-2.6723645219
H56	-2.0946603371	0.8802584216	-3.2800456444
H57	-2.5955829854	1.1802729057	-1.6195151982

(5) (THP)Mn(IV)F_2

F1	0.0153860231	0.0109099985	2.2719661557
Mn2	0.1834342069	-0.0084038891	4.0166006218
N3	-1.6257884879	0.8883138680	4.1988954583
N4	1.0795699669	1.8098704879	3.9529843547
N5	1.9936916143	-0.9052378095	3.8334396830
N6	-0.7110235893	-1.8271682854	4.0837411679
C7	-0.9057631404	3.2366259293	4.1882255328
C8	3.4146147412	1.0934470283	3.6910099140
C9	1.2806841918	-3.2542989046	3.9143843995
C10	-3.0525956398	-1.1098286093	4.2754275811
C11	0.4584379560	3.0285670751	4.0472518704
C12	2.4215124304	2.0543284804	3.8114546374
C13	3.2064362785	-0.2779490315	3.7060744875
C14	2.2372050708	-2.2544977255	3.8174811095
C15	-0.0854348885	-3.0462124817	4.0339451951
C16	-2.0562739025	-2.0712250168	4.1888020455
C17	-2.8424897624	0.2613140766	4.2811024543
C18	-1.8656507145	2.2373101539	4.2510736209
C19	-3.2830878690	2.4695670113	4.3731997149
C20	-3.8864536205	1.2494329494	4.3889907452
H21	-3.7401250953	3.4483365619	4.4352592448
H22	-4.9408143871	1.0199288601	4.4688215569
C23	-2.2873591803	-3.4940203894	4.2048267466
C24	-1.0699975920	-4.0961364941	4.1122135274
H25	-3.2631813676	-3.9552145811	4.2807235346
H26	-0.8407198355	-5.1533914457	4.0941297615
C27	2.6546448958	3.4768335185	3.8155623639
C28	1.4425247387	4.0785262555	3.9634696758
H29	3.6286403865	3.9380215660	3.7187976938
H30	1.2160998264	5.1354808162	4.0111636913
C31	3.6526028108	-2.4865544561	3.6752325845
C32	4.2508472041	-1.2660055999	3.6037703273
H33	4.1117134436	-3.4654497744	3.6350484809
H34	5.3025561546	-1.0364280145	3.4948572379
H35	1.6281539587	-4.2812542830	3.8868947645
H36	4.4364081446	1.4421487143	3.5858575871
H37	-1.2504381283	4.2633206784	4.2442725275
H38	-4.0770985977	-1.4581818925	4.3511376037

F39	0.3504485068	-0.0277399322	5.7610718094

(6) (THP)Mn(IV)(F)(OH)

F1	-0.0111681815	0.0199644255	2.2634966018
Mn2	0.1898145435	-0.0109400886	4.0251379313
N3	-1.6205064320	0.8847701921	4.2529195716
N4	1.0784089848	1.8160197582	3.9308773156
N5	1.9922432803	-0.9021992524	3.8488385842
N6	-0.7191339114	-1.8311555052	4.0651650182
C7	-0.9041520545	3.2381834260	4.1978569446
C8	3.4107653901	1.0962292036	3.6788001063
C9	1.2763910897	-3.2520645995	3.9205792708
C10	-3.0565211368	-1.1125389273	4.2671466085
C11	0.4584853804	3.0331272704	4.0331865923
C12	2.4181369869	2.0597585777	3.7871066449
C13	3.2036746812	-0.2755519521	3.7139905372
C14	2.2341894565	-2.2514391276	3.8361233151
C15	-0.0924072245	-3.0477853389	4.0212186256
C16	-2.0629849183	-2.0762436707	4.1646079752
C17	-2.8436377671	0.2589178229	4.3024616857
C18	-1.8629642728	2.2376733299	4.2829455171
C19	-3.2802329126	2.4688707505	4.3865897450
C20	-3.8854463749	1.2480890069	4.3955147289
H21	-3.7393900062	3.4475000631	4.4338307243
H22	-4.9418634050	1.0214340636	4.4539898742
C23	-2.2951764184	-3.5007729244	4.1714435630
C24	-1.0770463037	-4.1010346826	4.0863599770
H25	-3.2712418412	-3.9631152089	4.2378118159
H26	-0.8465571528	-5.1580817121	4.0657510838
C27	2.6523932146	3.4839353784	3.7840911859
C28	1.4419748435	4.0855069395	3.9387486033
H29	3.6257931519	3.9447996547	3.6800614286
H30	1.2155552381	5.1425305307	3.9855873453
C31	3.6499782007	-2.4846288782	3.6947478503
C32	4.2484322815	-1.2643302698	3.6163857607
H33	4.1089644985	-3.4637179210	3.6557091719
H34	5.2998775560	-1.0358725581	3.5022092569
H35	1.6263751727	-4.2784883939	3.8940095929
H36	4.4328007376	1.4427520372	3.5680902016
H37	-1.2517864586	4.2647747003	4.2481644402
H38	-4.0830508413	-1.4581836478	4.3284962540
O39	0.4000101619	-0.0495639542	5.8229043018
H40	-0.4064028915	0.2720470494	6.2516040841

(7) (THP)Mn(III)(F) – fluorocyclohexane (axial)

F1	0.9204886821	-0.4470187578	1.5856156371

Mn2	0.3575135774	-0.0690522770	4.2566075018
N3	-1.3110313532	0.8922403078	3.5589535863
N4	1.4229938841	1.6481669362	3.9845605383
N5	2.1136126199	-1.0937522389	4.4441680267
N6	-0.6212659802	-1.8485341449	4.0242073504
C7	-0.4168276448	3.1757248253	3.4194055365
C8	3.6688096866	0.8047006528	4.5115226120
C9	1.2331870337	-3.3849759487	4.5109556450
C10	-2.8753789282	-1.0009633164	3.5360953005
C11	0.9114880511	2.8924185052	3.7122847011
C12	2.7656616601	1.8173211234	4.2133135999
C13	3.3613287420	-0.5468488801	4.6050710564
C14	2.2564007805	-2.4495501832	4.5975272393
C15	-0.1001091250	-3.0992356306	4.2442861504
C16	-1.9676187058	-2.0167468726	3.8114537512
C17	-2.5631453355	0.3476723618	3.4121087796
C18	-1.4444583397	2.2426810417	3.3498591991
C19	-2.8188117309	2.5562223579	3.0472910312
C20	-3.5114165738	1.3837746279	3.0881575648
H21	-3.1915548295	3.5499719371	2.8356426045
H22	-4.5672287919	1.2203840944	2.9154969979
C23	-2.3031629218	-3.4164405424	3.8910441107
C24	-1.1471019488	-4.0860815084	4.1563991925
H25	-3.2982233924	-3.8199368208	3.7558900245
H26	-1.0010065033	-5.1503801027	4.2846033617
C27	3.1117906447	3.2105450971	4.0780403695
C28	1.9648207940	3.8753938767	3.7667442897
H29	4.1088182646	3.6118785818	4.2042615208
H30	1.8279101062	4.9336722179	3.5866392414
C31	3.6383224093	-2.7681191467	4.8599140424
C32	4.3218532442	-1.5904597613	4.8665624655
H33	4.0206641240	-3.7684984282	5.0154636351
H34	5.3795262984	-1.4275385420	5.0276110059
H35	1.4979041399	-4.4267944491	4.6603585318
H36	4.7040777398	1.0912236096	4.6658237826
H37	-0.6733687943	4.2128645134	3.2284904787
H38	-3.9120450858	-1.2867840110	3.3918839732
C39	0.4595221628	-1.8972157977	-0.2402180269
C40	-0.1977551759	0.5613270241	-0.2578380593
C41	1.7458952497	-1.5563767136	-1.0109087635
H42	-0.3350283800	-2.1855990015	-0.9428105995
H43	0.6169061046	-2.7490382737	0.4309738275
C44	1.0898031241	0.8960759393	-1.0291051773
H45	-1.0281593012	0.4048375836	-0.9607056482
H46	-0.4872058666	1.3864445087	0.4020096186
C47	1.5661412533	-0.2968428006	-1.8745448016

H48	2.0457418234	-2.4091726446	-1.6312829193
H49	2.5545284432	-1.3894969979	-0.2886159593
H50	0.9262910638	1.7757639911	-1.6627171352
H51	1.8710783150	1.1657673134	-0.3076758621
H52	2.5060919615	-0.0493001082	-2.3827466320
H53	0.8287206823	-0.5001251308	-2.6655495742
C54	-0.0451638042	-0.7089882944	0.5731306511
H55	-0.9721600542	-0.9527371379	1.1004847407
F56	0.0051064513	0.1532338960	6.0551147847

(8) (THP)Mn(III)(F) – fluorocyclohexane (equatorial)

F1	-0.0927071760	0.0308067708	1.4404105197
Mn2	0.2018815132	-0.0059517811	4.2444605467
N3	-1.6297464763	0.8956502697	4.1736714241
N4	1.0708645077	1.8123857588	3.9068019166
N5	1.9793452353	-0.9009242318	3.7812082448
N6	-0.7213759036	-1.8177438530	4.0456369631
C7	-0.9131254555	3.2438955848	4.1154068378
C8	3.4048424496	1.0944439684	3.6466910953
C9	1.2605527315	-3.2492127543	3.8127011278
C10	-3.0583529318	-1.0991699514	4.2808349370
C11	0.4524164809	3.0357416485	3.9707791574
C12	2.4127047970	2.0598559252	3.7583479450
C13	3.1957366692	-0.2787330867	3.6510826878
C14	2.2222850965	-2.2506737743	3.7263674856
C15	-0.1055406660	-3.0409117863	3.9533820427
C16	-2.0663160149	-2.0647661293	4.1654654860
C17	-2.8491618729	0.2741212092	4.2770535448
C18	-1.8750122528	2.2458093631	4.2022343373
C19	-3.2920534276	2.4828007111	4.3230265873
C20	-3.8951099499	1.2623624768	4.3691491969
H21	-3.7509500309	3.4621485129	4.3633982496
H22	-4.9499404480	1.0359181663	4.4552989826
C23	-2.3059392047	-3.4862923240	4.1425569964
C24	-1.0922016603	-4.0905522668	4.0116785709
H25	-3.2824996506	-3.9469878882	4.2163554770
H26	-0.8696132703	-5.1482120885	3.9559023519
C27	2.6464229709	3.4820658579	3.7223425523
C28	1.4329490559	4.0862555987	3.8536436179
H29	3.6188447632	3.9431730940	3.6082718129
H30	1.2062887419	5.1443981478	3.8693753581
C31	3.6339235220	-2.4863506059	3.5518692623
C32	4.2364027910	-1.2657703029	3.5053469733
H33	4.0895433422	-3.4649614066	3.4742755680
H34	5.2872237258	-1.0384132484	3.3816101405
H35	1.6039423425	-4.2771718548	3.7553276289

H36	4.4270848744	1.4418265773	3.5365771014
H37	-1.2582490834	4.2718017368	4.1532288287
H38	-4.0827308347	-1.4462664042	4.3711296252
F39	0.3913942480	-0.0286540002	6.0790325480
C40	-0.1980074265	0.0284602847	0.0348802993
C41	-0.2500048792	-1.4141550688	-0.4521456896
C42	-1.4369611767	0.8192345372	-0.3662208752
H43	0.7071110415	0.5240579288	-0.3432195361
C44	-0.4438324237	-1.4642113708	-1.9785714444
H45	-1.0891564662	-1.9130406004	0.0502761823
H46	0.6641183539	-1.9377514534	-0.1510148043
C47	-1.6362316814	0.7779885178	-1.8922070166
H48	-2.3038204440	0.3729389817	0.1386510010
H49	-1.3488807204	1.8502225046	-0.0058496906
C50	-1.6860284275	-0.6682134326	-2.4134840741
H51	-0.5194918189	-2.5063975439	-2.3095849811
H52	0.4451874661	-1.0465849979	-2.4729140966
H53	-2.5523954873	1.3158945305	-2.1619467070
H54	-0.8089379291	1.3112742210	-2.3824404335
H55	-1.7754493869	-0.6735592855	-3.5064491914
H56	-2.5866557530	-1.1622844520	-2.0222489367

(9) (THP)Mn(III)(OH) – fluorocyclohexane (axial)

F1	0.8255532258	-0.5073439218	1.5912918239
Mn2	0.3418420107	-0.0722248105	4.2675535832
N3	-1.3687438085	0.8416522836	3.6126531203
N4	1.3522493689	1.6773088166	3.9549984922
N5	2.1262250510	-1.0551387494	4.3720352032
N6	-0.6016329610	-1.8871257698	4.0655092246
C7	-0.5467301040	3.1533412611	3.4683555990
C8	3.6326492393	0.8851243466	4.3954862280
C9	1.3117106830	-3.3712329519	4.4688182208
C10	-2.8832714805	-1.0947615744	3.6221262937
C11	0.7996870919	2.9080404230	3.7115350761
C12	2.6961999551	1.8786205930	4.1361219513
C13	3.3629915063	-0.4743217460	4.4934041303
C14	2.3107345036	-2.4067533558	4.5195047509
C15	-0.0389520782	-3.1257418719	4.2490325924
C16	-1.9455794678	-2.0910616415	3.8711024016
C17	-2.6092161602	0.2625001641	3.4992256768
C18	-1.5475978972	2.1898008768	3.4241082121
C19	-2.9398342755	2.4667921000	3.1679848429
C20	-3.5969203029	1.2750948976	3.2161635514
H21	-3.3467268375	3.4516059998	2.9787405106
H22	-4.6524600328	1.0828747451	3.0738092776
C23	-2.2402002698	-3.5004216785	3.9413786506

C24	-1.0594378533	-4.1408153280	4.1723245359
H25	-3.2256552037	-3.9313504106	3.8206580096
H26	-0.8812596345	-5.2026423225	4.2794923246
C27	3.0030398418	3.2815564683	3.9986156981
C28	1.8286131379	3.9191195070	3.7357546340
H29	3.9935893993	3.7076334374	4.0907006399
H30	1.6589985526	4.9750623998	3.5698172924
C31	3.7096845533	-2.6874859208	4.7366621967
C32	4.3603841234	-1.4919582117	4.7215499208
H33	4.1241330245	-3.6771802368	4.8782613758
H34	5.4180505782	-1.2998905552	4.8468505222
H35	1.6132856157	-4.4050059591	4.6020085009
H36	4.6654269031	1.1955027308	4.5151902242
H37	-0.8416202525	4.1836936838	3.2967209390
H38	-3.9157864508	-1.4049795001	3.4987040832
C39	0.1144323250	-1.7285256968	-0.3176563570
C40	0.2119321554	0.8134800252	-0.2886164334
C41	1.5137463113	-1.7735084186	-0.9540157576
H42	-0.6574947768	-1.7523865060	-1.0996982994
H43	-0.0534229628	-2.5998501551	0.3253057784
C44	1.6110425033	0.7659261893	-0.9248833868
H45	-0.5552621789	0.9133034865	-1.0693883803
H46	0.1099323941	1.6796236465	0.3745119682
C47	1.8016807421	-0.5034153223	-1.7726004806
H48	1.6093614718	-2.6664134716	-1.5829560938
H49	2.2589651590	-1.8672762891	-0.1545090172
H50	1.7750718910	1.6630599361	-1.5333192462
H51	2.3606543547	0.7844487957	-0.1241892191
H52	2.8206956213	-0.5381189048	-2.1769224204
H53	1.1242233371	-0.4676762460	-2.6389254590
C54	-0.0876114691	-0.4569931908	0.5021021658
H55	-1.0868741111	-0.4228741669	0.9477187126
O56	0.0659149419	0.1872248099	6.1390362277
H57	-0.2968908193	-0.5462707329	6.6513177127

(8) (THP)Mn(III)(OH) – fluorocyclohexane (equatorial)

F1	-0.8378914254	-0.2570688714	1.6326490119
Mn2	0.1220065388	-0.0558628037	4.2220494085
N3	-1.6609877670	0.8606767610	4.4672985447
N4	0.8962931210	1.7573298198	3.5058558985
N5	1.7509639685	-0.9881233208	3.4556709084
N6	-0.8313391825	-1.8878307345	4.3325077414
C7	-1.0159284005	3.1971881681	4.0047281490
C8	3.1231575116	0.9762083391	2.8624888281
C9	1.0602895733	-3.3331484378	3.7775563594
C10	-3.0399391120	-1.1041282053	5.0291900865
C11	0.2883402313	2.9827043610	3.5704301659

C12	2.1735920397	1.9742026391	3.0603299001
C13	2.9187652145	-0.3880966593	3.0434274890
C14	1.9814056834	-2.3438608214	3.4503401451
C15	-0.2537847000	-3.1173339630	4.1764533590
C16	-2.1153389738	-2.1041300624	4.7509490458
C17	-2.8243403041	0.2622863583	4.8887562601
C18	-1.9082744767	2.2125915398	4.4152326262
C19	-3.2656651179	2.4722571517	4.8278915393
C20	-3.8300377874	1.2687181959	5.1215608085
H21	-3.7171592196	3.4548728439	4.8713996500
H22	-4.8388452748	1.0620464689	5.4533624051
C23	-2.3642009864	-3.5233112690	4.8542560081
C24	-1.2098210985	-4.1515497036	4.4965527403
H25	-3.3034518509	-3.9664214629	5.1589090524
H26	-1.0099129052	-5.2138963695	4.4497429201
C27	2.3782468875	3.3840391391	2.8265156030
C28	1.2079758073	4.0091906779	3.1408637337
H29	3.2991170670	3.8255690577	2.4676904258
H30	0.9778725353	5.0654927859	3.0925616414
C31	3.3329425303	-2.6044011543	3.0214508779
C32	3.9120731943	-1.3972301876	2.7730490608
H33	3.7668456123	-3.5908870677	2.9224333858
H34	4.9166932972	-1.1922518307	2.4275313486
H35	1.3978013046	-4.3621186915	3.7080954000
H36	4.1052204685	1.2843475110	2.5183745753
H37	-1.3752600785	4.2211697597	4.0167353909
H38	-4.0247417762	-1.4150551672	5.3621763257
O39	0.7243871339	0.0591413372	6.0136485437
H40	1.0735946783	0.9100987839	6.3077280003
C41	-0.0918767748	-0.0573253043	0.4485818678
C42	0.0725904600	-1.3972094397	-0.2577580204
C43	-0.8179614915	0.9677815678	-0.4131508616
H44	0.8840603019	0.3305933011	0.7639071586
C45	0.8042451337	-1.2145687017	-1.6000739819
H46	-0.9267095347	-1.8190058962	-0.4303738922
H47	0.6106465023	-2.0924824869	0.3955068920
C48	-0.0901149252	1.1575335068	-1.7559108712
H49	-1.8403080684	0.6066283639	-0.5881355965
H50	-0.8972265326	1.9151594864	0.1314905683
C51	0.0949018524	-0.1806458868	-2.4905349693
H52	0.8807914444	-2.1784763138	-2.1162290683
H53	1.8350750349	-0.8826209524	-1.4101648432
H54	-0.6440384434	1.8665657950	-2.3820058252
H55	0.8952685051	1.6103110919	-1.5744135033
H56	0.6596832120	-0.0279965623	-3.4181546634
H57	-0.8899541581	-0.5710176336	-2.7840292739

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27. The need for both AgF and tetrabutyammonium fluoride apparently derives from the limited solubility of AgF in the reaction medium and the need for a higher fluoride ion concentration than can be maintained by AgF alone. The UV-visible λ_{max} observed for (TMP)Mn^{III}-Cl (**1**) (475 nm) changed immediately to that of a mixture of (TMP)Mn^{III}-F (453 nm) and $[(TMP)Mn^{III}(F)_2]^-$ (440 nm) under the reaction conditions.

28. The high selectivity for monofluorination, the low reactivity of C-H bonds near carbonyl groups, and the limited reactivity of the solvents as well as the tetrabutylammonium ion seem to reflect a very strong polar effect in the C-H bond cleavage step in this reaction.

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